

PATENT SPECIFICATION

(11) 1 513 672

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- (21) Application No. 20686/75 (22) Filed 15 May 1975
 (31) Convention Application No. 70096
 (32) Filed 16 May 1974
 (31) Convention Application No. 71849
 (32) Filed 14 Feb. 1975 in
 (33) Luxembourg (LU)
 (44) Complete Specification published 7 June 1978
 (51) INT CL² C08G 73/02; A61K 7/06, 7/13, 7/40; C08L 79/02; C11D 3/37

(52) Index at acceptance
 C3R 35C 35D1 35D2 35D3 35D4 35P2 C11 C12 C16 C25 C29
 C4 C6X C9A L2A L2B L2X
 A5B 771 774
 C5D 6A1 6A3 6A8A 6B11C 6B12B3 6B12F1 6B12N2
 6B12N3 6B12P 6B13 6B1 6B2 6C8
 D1B 2A4

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(54) COSMETIC COMPOSITIONS BASED ON QUATERNISED POLYMERS

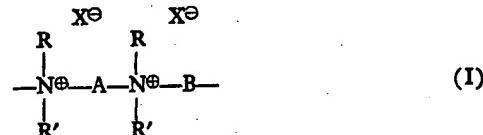
(71) We, L'OREAL, a French Body Corporate of 14, Rue Royle Paris 75008, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the use in cosmetics of polymers possessing quaternised ammonium groups, to the cosmetic compositions containing these polymers, and to a process for treating hair or skin using these polymers.

Certain cationic polymers wherein the quaternised nitrogen atoms form part of the macro-chain are known and their use as pesticides, as flocculating agents, as surface-active agents and as ion exchangers has already been proposed.

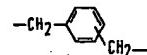
It has now been discovered that, surprisingly, such polymers exhibit valuable cosmetic properties if they are applied to the hair or to the skin.

According to the present invention there is provided a method of treating the hair and/or the skin which comprises applying thereto at least one quaternised polymer comprising recurring units of the general formula I:



in which

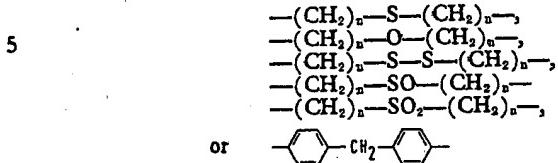
X[⊖] represents an anion derived from an inorganic or organic acid, R is a lower (C₁ to C₅) alkyl group or a —CH₂—CH₂OH group, R' is an aliphatic radical, an alicyclic radical or an araliphatic radical, which radical contains at most 20 carbon atoms, or two radicals R and R' attached to the same nitrogen atom form, with the latter, a ring which can contain a second hetero-atom other than nitrogen, A represents a divalent group of the formula



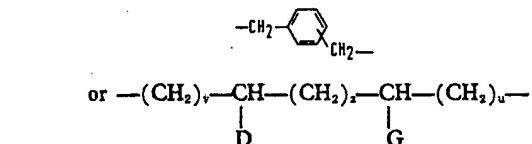
or —(CH₂)_x—CH—(CH₂)_y—CH—(CH₂)_t—

in which x, y and t are each independently 0 or an integer which can vary from 1 to

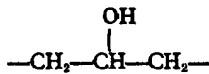
11 and are such that the sum $(x+y+t)$ is greater than or equal to 0 and less than 18, and E and K represent a hydrogen atom or an aliphatic radical having fewer than 18 carbon atoms, or A represents a divalent group of the formula:



10 n being an integer equal to 2 or 3, B represents a divalent group of the formula



in which D and G represent a hydrogen atom or an aliphatic radical having fewer than 18 carbon atoms, and v, z and u are each independently 0 or an integer which can vary from 1 to 11, and any two of them can simultaneously be 0, but the sum $(v+z+u)$ is greater than or equal to 1 and less than 18 and the sum $(v+z+u)$ is greater than 1 if the sum $(x+y+t)$ is 0, or B represents a divalent group of the formula

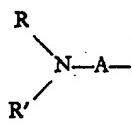


20 or $-(CH_2)_n-O-(CH_2)_n-$,

n being defined as above.
Certain polymers of the formula I are known whilst others are new (as indicated

The polymers of which the recurring units correspond to the formula I will, for simplicity, be referred to by the expression "polymers of formula I".

The terminal groups of the polymers of the formula I vary depending on the relative proportions of the starting reactants. They can be either of the type

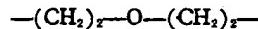


or of the type

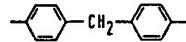
In the general formula I, X^{\ominus} especially represents a halide, (bromide, iodide or chloride) anion or an anion derived from other inorganic acids, such as phosphoric acid or sulphuric acid, or an anion derived from an organic sulphonate or carboxylic acid, especially an alkanoate acid having 2 to 12 carbon atoms (for example acetic acid), a phenylalkanoate acid (for example phenylacetic acid), benzoic acid, lactic acid, citric acid or para-toluenesulphonate acid; the substituent R preferably represents an alkyl group having 1 to 6 carbon atoms; if R' represents an aliphatic radical, it is in particular an alkyl or cycloalkyl-silyl radical having fewer than 20 carbon atoms and preferably not having more than 16 carbon atoms; if R' represents an alicyclic radical, it is especially a cycloalkyl radical with 5 or 6 ring members; if R₁ represents an araliphatic radical, it is especially an aralkyl radical, such as a phenylalkyl radical, of which the alkyl group preferably comprises from 1 to 3 carbon atoms; if two radicals R and R' attached to one and the same nitrogen atom form a ring therewith, R and R' can together especially represent a polymethylene radical having 2 to 6 carbon atoms, and the ring can contain a second hetero-atom, for example oxygen or sulphur; if the substituent E, K, D or G is an aliphatic radical, it is especially an alkyl radical having

1 to 17 carbon atoms and preferably 1 to 12 carbon atoms; v, z and u are preferably from 1 to 5, but two of them can be zero; x, y and t are preferably from 0 to 5; if A or B represents axylylene radical, it can be an o-, m- or p-xylylene radical.

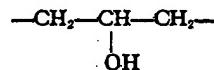
5 Amongst the polymers of the formula I, the preferred compounds for the cosmetic use according to the invention are especially those for which R is a methyl or hydroxyethyl radical, R' is an alkyl radical having 1 to 16 carbon atoms, a benzyl radical or a cyclohexyl radical, or R and R' together represent the $-(CH_2)_5-$ or



10 radical; A is a xylylidene radical, a polymethylene radical having 2 to 12 carbon atoms and optionally branched by one or two alkyl substituents having 1 to 12 carbon atoms, a radical of the formula



15 or a polymethylene radical having 4 or 6 carbon atoms and containing a hetero-atom grouping of the type of $-O-$, $-S-$, $-S-S-$, $-SO-$ or $-SO_2-$; B is a xylylidene radical, a polymethylene radical having 3 to 10 carbon atoms and optionally substituted by one or two alkyl radicals having 1 to 12 carbon atoms, a



radical, or a polymethylene radical having 4 or 6 carbon atoms and containing an oxygen hetero-atom; and X is a chlorine, iodine or bromine atom.

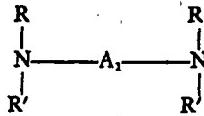
20 It should be noted that the groups A, B, R or R' can have several different values in one and the same polymer I.

Such polymers can be obtained as indicated later in describing the processes of preparation of the polymers of formula I. By way of illustration, the preparation of one such polymer is described in Example 43.

25 The polymers of formula I can, in particular, be prepared in accordance with the conventional processes reviewed below:

PROCESS 1.

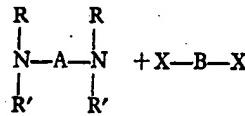
This process consists of carrying out a polyquaternisation reaction of a di-tertiary diamine of the formula



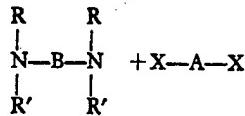
30 with a dihalide of the formula X-B₁-X, in which R, R' and X have the meanings indicated above; A₁ represents A if B₁ represents B, and A₁ represents B if B₁ represents A, the groups A and B being as defined above.

35 This process for the preparation of the polymers of the formula II can thus be carried out in accordance with one of the two following methods:

PROCESS 1A.

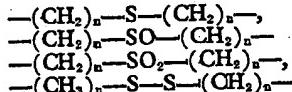


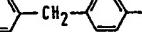
PROCESS 1b.



If A represents one of the following groups:

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or 

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Process 1a is preferably used.

The polyquaternisation reaction is carried out, for example, in a solvent or a mixture of solvents which favours quaternisation reactions, such as water, dimethylformamide, acetonitrile and the lower alcohols, especially the lower alkanols such as methanol.

The reaction temperature is suitably from 10° to 150° C. and preferably from 20° to 100° C.

The reaction time depends on the nature of the solvent, on the starting reactants and on the desired degree of polymerisation.

In general, the starting reactants are reacted in equimolecular amounts but it is also possible to use either the diamine or the dihalide in a slight excess, this excess being generally less than 20 mol%.

The resulting polycondensate can be isolated at the end of the reaction, either by filtration or by concentrating the reaction mixture.

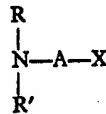
It is possible to regulate the average chain length by adding, at the start or in the course of the reaction, a small amount (e.g. 1 to 15 mol% relative to one of the reactants) of a monofunctional reagent such as a tertiary amine or a monohalide. In this case, at least a part of the terminal groups of the resulting polymer I consists either of the tertiary amine group used or of the hydrocarbon group of the monohalide. Examples of limiting the chain length by adding varying amount of triethylamine are given later (see Examples 47 to 49).

This invention includes the use of the polymers of the formula I which have such terminal groups.

In place of the starting reactant it is also possible to use either a mixture of di-tertiary diamines or a mixture of dihalides or a mixture of di-tertiary amines and a mixture of dihalides, provided the ratio of the total molar amounts of diamines and dihalides is about 1. This possibility is illustrated later in Example 43.

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PROCESS 2.
This process consists of subjecting a ω -halogenated tertiary amine of the formula



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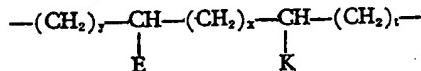
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to a self-polyquaternisation reaction.

In this case, the polymer obtained corresponds to the general formula I, in which B=A, with R, R' and X having the meanings mentioned above, and A can only assume the meaning

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the sum (x+y+z) having to be greater than 4.

The reaction can be carried out either without solvent or with the same solvents as in Process I, using the same ranges of reaction temperature. As before, it is possible to add a monofunctional reagent to regulate the degree of polyquaternisation.

It is also possible to use a mixture of several tertiary ω -halogenated amines.

In the two processes for the preparation of the polymers of the formula I mentioned above, the polymer which results can be isolated at the end of the reaction either by filtration or by concentrating the reaction mixture and crystallising the product, if appropriate, by adding a suitable anhydrous organic liquid, for example acetone.

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The di-tertiary diamines used as starting products in the above Process 1 can be prepared in accordance with one of the methods indicated below.

Method 1:

A primary amine of the formula $R-NH_2$ is reacted with a dihalide of the formula $Hal-A_1-Hal$, Hal being a halogen atom and preferably a bromine or iodine atom. The process is suitably carried out at 50° to 150° C, using an excess of primary amine, generally 2 to 5 mols of primary amine per mol of dihalide. After adding to the reaction mixture a basic solution, for example a solution of sodium hydroxide or potassium hydroxide, the di-secondary diamine of the formula

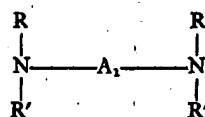
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is obtained. The latter is then subjected to an alkylation reaction according to known methods, the expression "alkylation" here denoting the replacement of a hydrogen atom linked to the nitrogen by a group R' as defined above. The di-tertiary diamine of the formula

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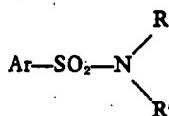
can then be isolated in accordance with the usual methods.

Method 2: (applicable to the case wherein A_1 is a xylidene radical or an alkylene radical).

A primary amine $R-NH_2$ is reacted with an arylsulphonyl halide $Ar-SO_2-Hal$, Ar being an aryl group, for example a phenyl or tolyl group, and Hal being a halogen atom, for example a chlorine atom. A sulphonamide of formula $Ar-SO_2-NHR$ is obtained, which is subjected to an alkylation reaction in accordance with known methods for producing a sulphonamide of the formula

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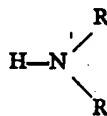
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which, on acid hydrolysis, for example by means of an aqueous solution of sulphuric acid, gives the secondary amine of the formula



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The latter is then reacted with a dihalide of the formula $Hal-A_1-Hal$ (Hal and A_1 being defined as above), in the presence of a tertiary amine such as N-ethyl-diisopropylamine, using at least two mols of secondary amine and of tertiary amine per mol of dihalide. The reaction is preferably carried out without a solvent and at a temperature of 50° to 130° C. At the end of the reaction, the mixture is taken up in water to dissolve the amine salts and the solution is extracted with a suitable solvent, for example ethyl acetate. The extracts are then washed with an aqueous alkaline solution (sodium hydroxide or potassium hydroxide), and then with water. The organic phase is then dried, after which the di-tertiary diamine is isolated either by distillation or by concentration under reduced pressure.

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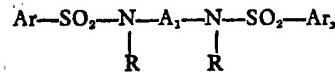
Method 3:

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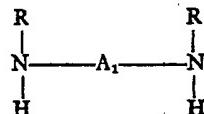
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A primary amine RNH_2 is reacted with an arylsulphonyl halide, as indicated in Method 2. The sulphonamide obtained, of the formula $Ar-SO_2-NHR$, is reacted with a dihalide of the formula $Hal-A_1-Hal$ at a temperature of, say, 80° to 140° C.

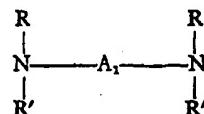
The disulphonamide formed, of the formula



can be subjected directly, without being isolated, to acid hydrolysis. This acid hydrolysis can be carried out, for example, in an 85% strength aqueous solution of sulphuric acid, at a temperature of, say, 120 to 145° C., for a period of, say, 7 to 20 hours. The di-secondary diamine of the formula



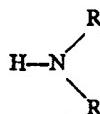
is obtained, and is subjected to an alkylation reaction, in accordance with known methods, so as to form the di-tertiary diamine of the formula



This method 3 is particularly useful in the case wherein $\text{A}_1=(\text{CH}_2)_n$, because it avoids the cyclisation side-reactions observed if methods 1 and 2 are used.

Method 4:

A secondary amine of the formula



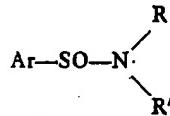
is reacted with a dihalide of the formula $\text{Hal}-\text{A}_1-\text{Hal}$ (Hal and A_1 being defined as indicated above) in the presence of an alkali metal carbonate or a tertiary amine such as N-ethyldiisopropylamine.

If the reaction is carried out in the presence of an alkali metal carbonate, at least one mol of carbonate is used per mol of dihalide and ethanol is generally used as the solvent; at the end of the reaction, the inorganic salts are filtered off, the ethanol is driven off under reduced pressure and the reaction products are separated by distillation.

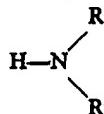
When the reaction is carried out in the presence of a tertiary amine, at least two mols of secondary amine and tertiary amine are used per mol of dihalide; the reaction is preferably carried out without a solvent and at a temperature of 50° to 130° C.; at the end of the reaction, the mixture is taken up in water to dissolve the amine salts and the solution is extracted with a suitable solvent, for example ethyl acetate; the extracts are then washed with an aqueous alkaline solution (sodium hydroxide or potassium hydroxide) and then with water; the organic phase is then dried and thereafter the di-tertiary diamine is isolated, for example by distillation or by concentration under reduced pressure.

The secondary amine starting materials (with $\text{R}'=-\text{CH}_2-\text{CH}_2-\text{OH}$) can be prepared by reaction of a halogen derivative $\text{R}-\text{Hal}$ with monoethanolamine.

The secondary amine starting materials (wherein R' is not $=-\text{CH}_2-\text{CH}_2-\text{OH}$) are obtained, for example, by reacting a primary amine of the formula $\text{R}-\text{NH}_2$ with an arylsulphonyl halide $\text{Ar}-\text{SO}_2-\text{Hal}$, Ar being an aryl group, for example a phenyl or tolyl group, and Hal being a halogen atom, for example a chlorine atom. A sulphonamide of the formula $\text{Ar}-\text{SO}_2-\text{NHR}$ is obtained, which is subjected to an alkylation reaction in accordance with the known methods, so as to form a sulphonamide of the formula

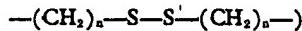


which, on acid hydrolysis, for example with an aqueous solution of sulphuric acid, gives the secondary amine of the formula

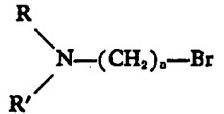


5 *Method 5:* (applicable to the case wherein A₁ represents —CH₂—CHOH—CH₂—) 5
 Epichlorohydrin is reacted with a secondary amine R—NH—R', preferably used in excess. The reaction is suitably carried out in a solution or suspension in water at a temperature of 40° to 100° C., with 3 to 10 mols of secondary amine per mol of epichlorohydrin. After adding to the reaction mixture a basic solution, for example a solution of sodium hydroxide or potassium hydroxide, and extracting with an appropriate solvent (for example ethyl acetate), a mixture of secondary amine starting material and di-tertiary diamine is obtained, which is separated by distillation.

10 *Method 6:* (applicable to the case wherein A₁ represents

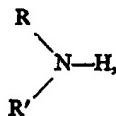


15 An alkali metal thiosulphate is reacted with an amine of the formula 15

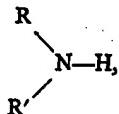


20 to form a Bünte salt, which is hydrolysed to the disulphide by means of a solution of sodium hydroxide or potassium hydroxide. The reaction is suitably carried out in water at a temperature of 40° to 100° C. When the Bünte salt has been formed completely, it is hydrolysed and the corresponding disulphide is extracted in an appropriate solvent such as ethyl acetate. The solvent can be removed by distillation under reduced pressure and the di-tertiarydiamine isolated and purified, if desired, by distillation under reduced pressure. 20

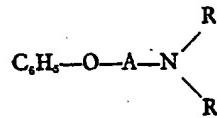
25 The ω-halogenated tertiary amines used as starting materials in Process 2 described above can themselves be prepared by applying processes described by M. R. LEHMAN, C. D. THOMPSON and C. S. MARVEL, J.A.C.S., 55, 1977 (1933) and by LITTMANN and MARVEL, J.A.C.S., 52, 287 (1930), replacing the dimethylamine starting material, as required, by the appropriate secondary amine of the formula 25



30 and R' being defined as above. They can also be obtained by the reaction, in the presence of a proton acceptor such as N-ethyldiisopropylamine, of a compound of the formula Br—A—OC₂H₅, with a secondary amine of the formula 30



35 in which A; R and R' are defined as above, followed by reaction with hydrobromic acid of the resulting compound of the formula 35



under the conditions described in the two J.A.C.S. references referred to above.

Though the invention is not limited to the use of polymers I having a degree of polymerisation varying within a particular range, it can be said that the polymers of the formula I which are most generally suitable have a molecular weight which is from 5,000 to 50,000.

They are generally soluble in at least one of the three following solvents: water, ethanol or a water-ethanol mixture.

It is possible to obtain films, which in particular exhibit good affinity to hair, by evaporation of the solution of the polymer.

As indicated above, the polymers of the formula I have valuable cosmetic properties which permit their use in the preparation of cosmetic compositions.

Such cosmetic compositions comprise polymers of the formula I either by way of the main active ingredient or by way of an additive.

These cosmetic compositions can be in the form of, for example, aqueous, alcoholic or aqueous-alcoholic solutions, (the alcohol being, in particular, a lower alkanol such as ethanol or isopropanol) or in the form of creams, gels or emulsions, or in the form of aerosol cans also containing a propellant.

Adjuvants generally present in the cosmetic compositions of the invention are, for example, perfumes, dyestuffs, preservatives, sequestering agents and thickeners.

The compositions suitable for application to the hair and/or skin which comprise at least one cosmetic adjuvant which is:

(i) a cosmetic resin such that the composition is in the form of a hair lacquer or wave-setting lotion;

(ii) a hair dye;

(iii) a hair restructuring agent;

(iv) a surface-active agent such that the composition is in the form of a shampoo; or

(v) an oil such that the composition is in the form of an emulsion for application to the skin, form another aspect of this invention.

It should be noted that the cosmetic compositions according to the invention can be either ready-to-use compositions or concentrates which have to be diluted before use. Hence, the cosmetic compositions of the invention are not restricted to a particular range of concentration of the polymer of the formula I.

In general, in the cosmetic compositions of the invention, the concentration of polymers of the formula I is from 0.5 to 10% by weight, preferably from 0.5 to 5% by weight.

The polymers of the formula I in particular have valuable cosmetic properties when applied to the hair.

Thus, if they are applied to the head of hair either by themselves or together with other active substances, in the course of a treatment such as shampooing, dyeing or wave-setting, they noticeably improve the properties of the hair.

For example, they assist the treatment and facilitate the combing out of wet hair. Even at a high concentration, they do not make wet hair sticky to the touch.

In contrast to the customary cationic agents, they do not make dry hair heavy and consequently facilitate bouffant hair styles. They make dry hair springy and give it a shiny appearance.

They contribute efficiently to removing the defects of hair which has been sensitised by treatments such as bleaching, permanent waving or dyeing. It is known, in fact, that sensitised hair is frequently dry, dull and rough, and difficult to comb out and set.

They are in particular of great value when they are used as pretreatment agents, especially before an anionic and/or non-ionic shampoo or before an oxidation dyeing which is itself followed by an anionic and/or non-ionic shampoo. The hair is then particularly easy to comb out and feels very soft.

They can also be used as pretreatment agents in other operations involving the treatment of hair, for example permanent wavings.

The cosmetic compositions for application to the hair can be in the form of, for example, aqueous, alcoholic or aqueous-alcoholic solutions (the alcohol generally being a lower alkanol such as ethanol or isopropanol), or in the form of creams, gels

or emulsions, or in the form of sprays. They can also be packaged in aerosol containers, which also contain a propellant, for example nitrogen, nitrous oxide or chlorofluorinated hydrocarbon of the "Freon" [Registered Trade Mark] type.

The adjuvants generally present in the cosmetic compositions for hair include perfumes, dyestuffs, preservatives, sequestering agents, thickeners and emulsifiers or resins usually employed in cosmetic compositions for hair (cosmetic resins).

The polymers of the formula I can be present in, for example, wavesetting lotions, treatment lotions and setting creams or gels, or as an additive in shampoo compositions, wavesetting compositions, permanent waving compositions, dyeing compositions, restructuring lotions, treatment lotions for counteracting dandruff, or hair lacquers.

The cosmetic compositions for hair according to the invention or used in the method of this invention, are thus in particular:

a) treatment compositions which comprise, by way of active ingredient, at least one polymer of the formula I in aqueous or aqueous-alcoholic solution.

The content of polymer of the formula I is generally from 0.5 to 10% by weight and preferably from 0.5 and 5% by weight.

The pH of these solutions is approximately 7 and can vary, for example, from 6 to 8. It is possible, if necessary, to bring the pH to the desired value by adding either an acid such as citric acid or a base, especially an alkanolamine such as monoethanolamine or triethanolamine.

In order to treat hair with such a lotion, the lotion is applied to wet hair and is allowed to act for, say, 3 to 15 minutes, and then the hair is rinsed.

If desired, a conventional wavesetting operation can then be carried out;

b) shampoos which comprise at least one polymer of the formula I and a cationic, non-ionic or anionic detergent.

The cationic detergents are, especially, long-chain quaternary ammonium compounds, esters of fatty acids and amino-alcohols, or polyether-amines.

The non-ionic detergents are especially esters of polyols and sugars, products resulting from the condensation of ethylene oxide with fatty compounds, with long chain alkyl-phenols, with long chain mercaptans or with long chain amides, and polyhydroxylic polyethers of a fatty alcohol.

The anionic detergents are especially alkali metal salts, ammonium salts or amine or amino-alcohol salts of fatty acids such as oleic acid, ricinoleic acid and acids from copra oil or from hydrogenated copra oil; alkali metal salts, ammonium salts or amino-alcohol salts of fatty alcohol sulphates, and especially of C₁₂—C₁₄ and C₁₂ fatty alcohols; alkali metal salts, magnesium salts, ammonium salts or amino-alcohol salts of oxyethyleneated fatty alcohol sulphates; products resulting from the condensation of fatty acids with isethionates, with taurine, with methyltaurine or with sarcosine; alkylbenzene-sulphonates, especially with a C₁₂ alkyl group; and alkylarylpolyether-sulphates or monoglyceride-sulphates. All these anionic detergents, as well as numerous others not mentioned here, are well known and are described in the literature.

These shampoos can also contain various adjuvants, for example perfumes, dyestuffs, preservatives, thickeners, foam stabilisers, softening agents or one or more cosmetic resins.

In these shampoos, the concentration of detergent is generally from 5 to 50% by weight and the concentration of polymer of the formula I or I_A is from 0.5 to 10%, and preferably from 0.5 to 5% by weight.

c) wavesetting lotions, especially for sensitised hair, which comprise at least one polymer of the formula I, in aqueous, alcoholic or aqueous-alcoholic solution.

They can also contain another cosmetic resin. The cosmetic resins which can be used in such lotions are very varied and are especially vinyl or crotonyl homopolymers or copolymers, for example polyvinylpyrrolidone, copolymers of vinylpyrrolidone and vinyl acetate and, copolymers of crotonic acid and vinyl acetate.

The concentration of the polymers of the formula I in these wavesetting lotions generally varies from 0.5 to 5% and preferably from 0.5 to 3% and the concentration of the other cosmetic resin varies essentially within the same proportions.

The pH of these wavesetting lotions is generally from 3 to 9 and preferably from 4.5 to 7.5. If desired, the pH can be changed, for example by adding an alkanolamine such as monoethanolamine or triethanolamine;

d) dyeing compositions for hair, which comprise at least one polymer of the formula I, a dyeing agent and a carrier.

The carrier is preferably chosen so as to form a cream.

The concentration of the polymers of the formula I in these dyeing compositions is generally from 0.5 to 15% by weight and preferably from 0.5 to 10% by weight.

In the case of oxidation dyeing, the dyeing composition can be packaged in two

parts, the second part comprising hydrogen peroxide. The two parts are mixed at the time of use.

Examples of such compositions and of their use are given in the working Examples.

5 e) hair lacquers, which comprise an alcoholic or aqueous-alcoholic solution of a customary cosmetic resin for lacquers, and at least one polymer of the formula I, this solution being placed in an aerosol container and mixed with a propellant.

10 It is possible, for example, to prepare an aerosol lacquer according to the invention by adding the customary cosmetic resin and the polymer of the formula I to a mixture of an anhydrous aliphatic alcohol such as ethanol or isopropanol and a liquefied propellant or a mixture of liquefied propellants such as halogenated hydrocarbons of the trichlorofluoromethane or dichlorodifluoromethane type.

15 In these hair lacquer compositions, the concentration of the cosmetic resin is generally from 0.5 to 3% by weight and the concentration of the polymer of the formula I is generally from 0.5 and 3% by weight.

15 Of course, it is possible to add adjuvants such as dyestuffs, plasticisers or any other customary adjuvant to these hair lacquers;

20 f) restructuring treatment lotions, which comprise at least one agent possessing hair restructuring properties and at least one polymer of the formula I.

20 The restructuring agents which can be used in such lotions are, for example, the methylol derivatives described in French Patents No. 1,519,979, 1,519,980, 1,519,981, 7,519,982 and 1,527,085.

25 In these lotions the concentration of the restructuring agent is generally from 0.1 to 10% by weight and the concentration of the polymer of the formula I is generally from 0.5 to 5% by weight.

25 g) Pretreatment compositions especially in the form of aqueous or aqueous-alcoholic solutions, optionally in an aerosol container, or in the form of creams or gels, these pretreatment compositions being intended to be applied to the hair before a shampoo and especially before an anionic and/or non-ionic shampoo, before an oxidation dyeing followed by an anionic and/or non-ionic shampoo, or before a permanent waving treatment.

30 In these pretreatment compositions, the polymer I forms the actual active ingredient and its concentration is generally from 0.5 to 10% and in particular from 0.5 to 5% by weight. The pH of these compositions which is near 7, generally from 3 to 9 and especially from 6 to 8.

35 These pretreatment compositions can contain various adjuvants (for example resins) usually employed in cosmetic compositions for hair including agents for changing the pH (for example, amino-alcohols such as monoethanolamine) as indicated for the compositions of paragraph a) above.

40 The polymers of the formula I also possess valuable cosmetic properties when they are applied to the skin.

40 In particular, they assist moisturising of the skin and thus prevent it from drying out. They also give the skin considerable softness to the touch.

45 The cosmetic compositions for the skin can be presented, for example in the form of creams, gels, emulsions or aqueous, alcoholic or aqueous-alcoholic solutions.

45 The concentration of the polymer of the formula I in these compositions for the skin is generally from 0.5 to 10% by weight.

50 The adjuvants generally present in these cosmetic compositions are, for example, perfumes, dyestuffs, preservatives, thickeners, sequestering agents and emulsifiers.

50 These compositions for the skin are, in particular, treatment creams or lotions for the hands or face, anti-sunburn creams, tinted creams, cleansing milks, and foaming bath liquids, or (are present) in deodorant compositions.

55 These compositions can be prepared in accordance with the usual methods.

For example, in order to prepare a cream, it is possible to emulsify an aqueous phase containing a solution of the polymer I and optionally other ingredients or adjuvants, and an oily phase.

60 The oily phase can consist of various products such as liquid paraffin, "Vaseline" [Registered Trade Mark] oil, sweet almond oil, avocado oil, olive oil and esters of fatty acids such as glyceryl monostearate, ethyl or isopropyl palmitate and alkyl myristates such as propyl, butyl or cetyl myristate. It is also possible to add fatty alcohols such as cetyl alcohol or waxes such as beeswax.

65 The polymers of the formula I can be present in the cosmetic compositions for the skin either as an additive or as the main active ingredient in treatment creams or lotions for the hands or face, or as an additive in compositions of anti-sunburn creams, tinted creams, cleansing milks and foam bath liquids.

The preferred polymers of the formula I are those described below in Examples No. 1 to 140.

In a particular embodiment of the invention the method for the treatment of hair consists of applying to the hair, before an anionic shampoo, or before an oxidation dyeing treatment followed by an anionic shampoo, at least one polymer of the formula I by means of a pretreatment composition as defined above.

The following Examples further illustrate the present invention.

EXAMPLES OF THE PREPARATION OF THE STARTING DIAMINES.

Preparation No. 1.

1,6-N,N'-Dibutyl-N,N'-dimethyl-diamino-hexane

61 g of 1-dibromohexane is added slowly, whilst stirring, to 91 g of n-butylamine previously brought to a temperature of 75° C. The temperature of the reaction mixture actually rises to 95° C. When the introduction is complete, the hydrobromide formed crystallises and the temperature rises to 110° C. The mixture is cooled to 60° C. and 250 cm³ of water and 50 cm³ of a concentrated aqueous solution of sodium hydroxide are introduced successively. Stirring is continued for ½ hour and then the precipitate of 1,6-N,N'-dibutyl-diamino-hexane is filtered off and dried under reduced pressure.
 b) 37 g of the latter product are added, with stirring and whilst keeping the temperature below +5° C., to a mixture of 108 g of pure formic acid and 11 g of water. 117 g of a 30% strength aqueous solution of formaldehyde are then introduced over the course of 10 minutes. The temperature is then raised slowly to 100° C. and the mixture is stirred at this temperature until carbon dioxide ceases to be evolved. The reaction mixture is then concentrated under reduced pressure and the residue is rendered alkaline by adding approximately 150 cm³ of a concentrated aqueous solution of sodium hydroxide. The mixture is extracted three times with 200 cm³ of isopropyl ether. The combined organic phases are washed three times with 100 cm³ of water, dried and concentrated. The residue is distilled in vacuo and 72 g of 1,6-N,N'-dibutyl-N,N'-dimethyl-diamino-hexane which distils at 98—99° C. under 0.1 mm of mercury, are collected.

Preparation No. 2.

1,3-N,N'-Dimethyl-N,N'-dioctyl-diamino-propane.

a) N-Methyl-octylamine.

523 g of octylamine benzenesulphonamide are dissolved in 1,500 cm³ of anhydrous xylene. 835 cm³ of a 2.4 N solution of sodium ethylate in ethanol are then introduced, with stirring, and the ethanol is then removed by distillation. Whilst keeping the stirred reaction mixture at 100—110° C., 385 cm³ of methyl sulphate are introduced over the course of 1 hour and the mixture is heated under reflux for 4 hours. After cooling, the inorganic salts are filtered off. 1,500 cm³ of a concentrated aqueous solution of sodium hydroxide are added to the filtrate, decanting is effected and the xylene phase is washed 4 times with 1,000 cm³ of water and then concentrated.

The residue obtained is added to a mixture of 1,400 g of concentrated sulphuric acid and 560 g of crushed ice and the whole is heated, with stirring, to 160° C. for 16 hours. After cooling, the reaction mixture is poured onto 3 kg of crushed ice and rendered alkaline by adding 3,500 cm³ of a concentrated aqueous solution of sodium hydroxide. The mixture is extracted three times with 2,000 cm³ of ethyl acetate, and the organic phases are washed with water, dried and concentrated under reduced pressure. The residue is distilled and the fraction which distils at 45—50° C. under 0.2 mm of mercury is collected.

b) 1,3-N,N'-Dimethyl-N,N'-dioctyl-diamino-propane.

69 g of 1,3-dibromo-propane are added to a mixture of 107 g of N-methyl-octylamine and 87.5 g of N-ethyl-diisopropylamine whilst keeping the temperature at 100—105° C. The mixture is then stirred for 7 hours at 120° C. and is cooled, and 500 cm³ of water and 200 cm³ of ether are added. The aqueous phase is decanted and the ether phase is treated with 50 cm³ of a concentrated aqueous solution of sodium hydroxide, decanted and washed three times with 100 cm³ of water. After drying, the ether is evaporated and then the starting N-methyl-octylamine which has not reacted. The residue obtained comprises two phases which are separated.

The clear upper phase is purified by distillation; 1,3-N,N'-dimethyl-N,N'-dioctyl-diamino-propane, which distils at 150—153° C. under 0.5 mm of mercury, is collected.

12

Preparation No. 3.

1,5-N,N'-Didecyl-N,N'-dimethyl-diamino-pentane.

a) 1,5-N,N'-Didecyl-diamino-pentane.

297 g of n-decylamine benzenesulphonamide are reacted with sodium ethylate in a manner analogous to that described in Example 2, in order to form the corresponding sodium derivative. After having removed the ethanol by evaporation, 162 g of 1,5-diiodopentane are introduced, with stirring, at a temperature of about 120° C. The mixture is kept at the reflux temperature of the xylene for 4 hours and is then cooled, and 500 cm³ of water are added with stirring in order to dissolve the inorganic salts formed.

The organic phase is then decanted, dried and concentrated under reduced pressure. The residue obtained is heated for 14 hours at 130° C. in the presence of 300 cm³ of 85% strength sulphuric acid. After cooling, the reaction mixture is poured onto 1.5 kg of crushed ice and is brought to pH 10 by adding a 30% strength aqueous sodium hydroxide solution. The precipitate formed is filtered off, washed with water and dried. 1,5-N,N'-Didecyl-diamino-pentane is obtained.

b) 1,5-N,N'-Didecyl-N,N'-dimethyl-diamino-pentane.

Methylation of the product obtained under a), in accordance with a method analogous to that described in Preparation No. 1, gives 1,5-N,N'-didecyl-N,N'-dimethyl-diamino-pentane. Boiling point = 193—195° C. (0.4 mm Hg).

Preparation No. 4.

1,3-N,N'-Didecyl-N,N'-dimethyl-diamino-propan-2-ol.

26.6 g of epichlorohydrin are added slowly to a vigorously stirred mixture of 370 g of N-methyl-dodecylamine and 600 cm³ of water. At the end of the addition, the reaction mixture is heated to 90° C. for 12 hours. After cooling, 10 cm³ of a concentrated aqueous sodium hydroxide solution are added and the mixture is extracted three times with 200 cm³ of ethyl acetate. The extraction solutions are dried over sodium sulphate and concentrated under reduced pressure. A first fraction corresponding to the excess N-methyl-dodecylamine is obtained; the second fraction, distilling at 235°—240° C. under 1.5 mm Hg is the di-tertiary diamine.

Preparation No. 5.

1,3-N,N'-Di-2-hydroxyethyl-N,N'-diethyl-diamino-propane.

A mixture consisting of 100 g of N-2-hydroxyethyloctylamine, 28.6 g of 1,3-dibromopropane, 22 g of potassium carbonate and 300 cm³ of ethanol is heated under reflux for 50 hours.

The inorganic salts are removed by filtration, the ethanol is distilled under reduced pressure and the residue is then distilled in vacuo. The expected diamine distils at 200—206° C. under 1 mm of mercury.

Preparation No. 6.

N-Butyl-N-methyl-2-aminoethyl disulphide.

44 g of N-butyl-N-methyl-2-bromoethylamine hydrobromide are dissolved in 10 cm³ of water. Thereafter the pH of the solution is adjusted to 7 by adding dilute sodium hydroxide whilst keeping the temperature at about 0° C. The temperature is then raised to 60° C. whilst introducing a solution of 43.7 g of sodium thiosulphate pentahydrate in 15.6 cm³ of water.

The reaction mixture is kept at 60° C. for 8 hours and then cooled, after which 71 cm³ of a concentrated aqueous sodium hydroxide solution are added. The mixture is left to stand for 2 hours, the organic phase is then extracted with 100 cm³ of ethyl acetate, and the extract is dried and concentrated under reduced pressure.

Distillation of the residue gives the expected diamine of boiling point = 140—150° C. (1.2 mm Hg).

The di-tertiary diamines indicated in Table I which follows were prepared analogously in accordance with the methods described previously; these di-tertiary diamines are used as starting materials in the examples of the preparation of polymers of the formula I, given later in the experimental part.

TABLE I

Preparation No.	Method No.	A ₁	R	R'
7	2	(CH ₂) ₁₀	CH ₃	C ₁₁ H ₂₅
8	1	(CH ₂) ₃	CH ₃	C ₄ H ₉
9	2	(CH ₂) ₆	CH ₃	C ₈ H ₁₇
10	2	(CH ₂) ₁₀	CH ₃	C ₈ H ₁₇
11	1	(CH ₂) ₁₀	CH ₃	C ₄ H ₉
12	2	(CH ₂) ₆	CH ₃	C ₁₆ H ₃₃
13	1	(CH ₂) ₆	CH ₃	cyclohexyl
14	1	(CH ₂) ₆	CH ₃	isobutyl
15	2	(CH ₂) ₃	CH ₃	C ₁₂ H ₂₅
16	2	(CH ₂) ₆	CH ₃	C ₁₂ H ₂₅
17	1	p-xylylene	CH ₃	C ₄ H ₉
18	1	m-xylylene	CH ₃	C ₄ H ₉
19	1	(CH ₂) ₁₂	CH ₃	C ₄ H ₉
20	1	(CH ₂) ₆	CH ₃	C ₄ H ₉
21	1	(CH ₂) ₆	CH ₃	isopropyl
22	1	(CH ₂) ₃	CH ₃	benzyl
23	1	-(CH ₂)—CH— CH ₃	CH ₃	C ₆ H ₁₃
24	1	(CH ₂) ₆	CH ₃	isobutyl
25	1	HC—(CH ₂) ₅ —CH CH ₃ CH ₂ —	CH ₃	C ₈ H ₁₇
26	1	—CH ₂ —CH—CH ₂ — C ₁₂ H ₂₅	CH ₃	C ₄ H ₉
27		CH ₂ —CH—CH ₂ OH	CH ₃	C ₁₀ H ₂₁
28		CH ₂ —CH—CH ₂ OH	CH ₃	C ₈ H ₁₇

TABLE I (continuation)

Preparation No.	Method No.	A ₁	R	R'
29		(CH ₂) ₃	-CH ₂ CH ₂ OH	C ₁₂ H ₂₅
30		(CH ₂) ₆	-CH ₂ CH ₂ OH	C ₁₂ H ₂₅
31		(CH ₂) ₆	-CH ₂ CH ₂ OH	C ₄ H ₉
32		(CH ₂) ₂ -S-S-(CH ₂) ₂	CH ₃	C ₁₂ H ₂₅
33		(CH ₂) ₂ -S-S-(CH ₂) ₂	CH ₃	C ₆ H ₁₇

EXAMPLES OF THE PREPARATION OF THE POLYMERS OF FORMULA I:

In all the examples which follow, the polymers are isolated, unless the contrary is indicated, by concentrating the reaction mixture under reduced pressure and drying in a vacuum (of the order of 0.1 mm of mercury) in the presence of phosphorus pentoxide. In Examples 1 to 73, the process used is Process 1a.

EXAMPLE 1. Polymer of the formula I (with R=R'=CH₃, A=(CH₂)₆, B=(CH₂)₃ and X=Br)

A solution consisting of 172.3 g of N,N,N',N'-tetramethyl-hexamethylenediamine and 202 g of 1,3-dibromopropane in 650 cm³ of a 50:50 mixture of methanol and dimethylformamide is stirred for 170 hours at ambient temperature.

A white precipitate is obtained on adding anhydrous acetone; it is filtered off and dried.

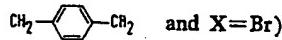
The polymer obtained contains 35.4% of Br.

EXAMPLE 2. Polymer of the formula I (with R=R'=CH₃, A=B=(CH₂)₆ and X=Br)

A solution of 172.3 g of N,N,N',N'-tetramethyl-hexamethylenediamine and 244 g of 1,6-dibromohexane in 1,600 cm³ of anhydrous methanol is heated under reflux for 24 hours, whilst stirring.

The polymer obtained contains 36.6% of Br.

It is water-soluble.

EXAMPLE 3. Polymer of the formula I (with R=R'=CH₃, A=(CH₂)₆, B=

A mixture of 116.2 g of N,N,N',N'-tetramethyl-ethylenediamine and 264 g of p-xylylidene bromide in 3,200 cm³ of anhydrous methanol is heated under reflux for 50 hours.

On cooling, a precipitate is obtained, which is filtered off and dried.

The resulting polymer contains 38.8% of Br.

It is soluble in water-ethanol mixtures.

EXAMPLE 4. Polymer of the formula I (with R=CH₃, R'=C₁₂H₂₅, A=(CH₂)₆, B=(CH₂)₆ and X=Br)

A solution of 438 g of N,N'-didodecyl-N,N'-dimethyl-trimethylenediamine and 244 g of 1,6-dibromohexane in 3,200 cm³ of anhydrous methanol is heated under reflux for 80 hours.

The resulting polymer contains 23.4% of Br.

It is soluble in ethanol.

EXAMPLE 5. Polymer of the formula I (with R=CH₃, R'=C₄H₉, A=(CH₂)₆, B=(CH₂)₁₀ and X=Br).

A solution of 256 g of N,N'-dibutyl-N,N'-dimethyl-hexamethylenediamine and 300 g of 1,10-dibromodecane in 3,200 cm³ of anhydrous methanol is heated under reflux for 45 hours.

The polymer obtained contains 25.0% of Br.

It is soluble in water and in ethanol.

EXAMPLE 6. Polymer of the formula I (with R=CH₃, R'=C₆H₁₁, A=(CH₂)₁₀, B=(CH₂)₄ and X=Br)

A solution consisting of 424 g of N,N'-dimethyl-N,N'-dioctyl-decamethylenediamine and 216 g of 1,4-dibromobutane in 3,200 cm³ of anhydrous methanol is heated under reflux for 60 hours.

The resulting polymer contains 21.1% of Br.

EXAMPLE 7. Polymer of the formula I (with R=CH₃, R'=C₆H₁₁, A=(CH₂)₉, B=(CH₂)₄ and X=Br)

A solution consisting of 326 g of N,N'-dimethyl-N,N'-dioctyl-trimethylenediamine and 216 g of 1,4-dibromobutane is heated under reflux for 60 hours.

The polymer obtained contains 26.0% of Br.

EXAMPLE 8. Polymer of the formula I (with R=CH₃, R'=C₁₂H₂₅, A=(CH₂)₁₀, B=(CH₂)₄ and X=Br)

A solution consisting of 537 g of N,N'-didodecyl-N,N'-dimethyl-decamethylenediamine and 216 g of 1,4-dibromobutane in 3,200 cm³ of anhydrous methanol is heated under reflux for 80 hours.

The polymer obtained contains 20.6% of Br.

It is soluble in ethanol.

EXAMPLE 9. Polymer of the formula I (with R=R'=CH₃, A=B=(CH₂)₁₀ and X=Br)

A solution obtained from 225 g of N,N,N',N'-tetramethyl-decamethylenediamine and 301 g of 1,10-dibromodecane in 3,200 cm³ of anhydrous methanol is heated under reflux for 25 hours.

The polymer obtained contains 28.0% of Br.

EXAMPLE 10. Polymer of the formula I (with R=CH₃, R'=C₆H₁₁, A=B=(CH₂)₉ and X=Br)

A solution consisting of 368 g of N,N'-dimethyl-N,N'-dioctyl-hexamethylenediamine and 244 g of 1,6-dibromoheptane in 3,200 cm³ of anhydrous methanol is heated under reflux for 40 hours.

The polymer obtained contains 24.3% of Br.

EXAMPLE 11. Polymer of the formula I (with R=CH₃, R'=C₆H₁₁, A=(CH₂)₉, B=

A mixture of 214 g of N,N'-dibutyl-N,N'-dimethyl-trimethylene, 5 g of p-xylylidene bromide in 1,800 cm³ of methanol is heated under reflux for 65 hours.

The polymer obtained contains 30.7% of Br.

It is soluble in water and in water-ethanol mixtures.

EXAMPLE 12. Polymer of the formula I (with R=CH₃, R'=C₆H₁₁, A=B=(CH₂)₁₀ and X=Br)

A solution of 312 g of N,N'-dibutyl-N,N'-dimethyl-decamethylenediamine and 301 g of 1,10-dibromodecane in 3,200 cm³ of anhydrous methanol is heated under reflux for 55 hours.

The polymer obtained contains 23.2% of Br.

It is soluble in water and in ethanol.

EXAMPLE 13. Polymer of the formula I (with R=R'=CH₃, A=(CH₂)₉, B=(CH₂)₄ and X=Br)

A solution consisting of 172.3 g of N,N,N',N'-tetramethyl-hexamethylenediamine and 216 g of 1,4-dibromobutane in 650 cm³ of a 50:50 mixture of methanol and dimethylformamide is stirred for 170 hours at ambient temperature.

On addition of anhydrous acetone, a white precipitate is obtained, which is filtered off and dried.

The polymer contains 36.6% of Br.

It is water-soluble.

EXAMPLE 14. Polymer of the formula I (with R=CH₃, R'=C₄H₉, A=(CH₂)₈, B=(CH₂)₄ and X=Br)

5 A solution of 214.4 g of N,N'-dibutyl-N,N'-dimethyl-trimethylenediamine and 216 g of 1,4-dibromobutane in 3,600 cm³ of anhydrous methanol is heated under reflux for 70 hours, whilst stirring.

The polymer obtained contains 32.8% of Br.
It is soluble in water and in ethanol.

EXAMPLE 15. Polymer of the formula I (with R=CH₃, R'=C₄H₉, A=B=(CH₂)₈ and X=Br)

10 A solution consisting of 256 g of N,N'-dibutyl-N,N'-dimethyl-hexamethylenediamine and 244 g of 1,6-dibromohexane in 3,600 cm³ of anhydrous methanol is heated under reflux for 40 hours.

The polymer contains 28.2% of Br.
It is soluble in water and in ethanol.

EXAMPLE 16. Polymer of the formula I (with R=CH₃, R'=C₁₂H₂₅, A=(CH₂)₈, B=(CH₂)₈ and X=Br)

15 A solution of 480.9 g of N,N'-didodecyl-N,N'-dimethyl-hexamethylenediamine and 202 g of 1,3-dibromopropane in a mixture of 2,000 cm³ of acetonitrile and 4,000 cm³ of isopropanol is heated under reflux for 30 hours.

20 The polymer formed contains 20.65% of Br.
It is soluble in ethanol and in water-ethanol mixtures.

EXAMPLE 17. Polymer of the formula I (with R=R'=CH₃, A=(CH₂)₈, B=(CH₂)₈ and X=Br)

25 A solution consisting of 130.2 g of N,N,N',N'-tetramethyl-trimethylenediamine and 244 g of 1,6-dibromohexane is heated under reflux for 55 hours.

The polymer formed contains 39.6% of Br.
It is soluble in water and in ethanol.

EXAMPLE 18. Polymer of the formula I (with R=R'=CH₃, A=(CH₂)₈, B=(CH₂)₈ and X=Br)

30 A solution consisting of 116.2 g of N,N,N',N'-tetramethyl-ethylenediamine and 244 g of 1,6-dibromohexane in 3,200 cm³ of anhydrous methanol is heated under reflux for 50 hours.

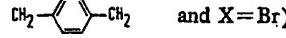
The polymer contains 41.9% of Br.
It is soluble in water and in water-ethanol mixtures.

EXAMPLE 19. Polymer of the formula I (with R=R'=CH₃, A=(CH₂)₈, B=(CH₂)₁₀ and X=Br)

35 A solution consisting of 116.2 g of N,N,N',N'-tetramethyl-ethylenediamine and 300 g of 1,10-dibromodecane in 3,200 cm³ of anhydrous methanol is heated under reflux for 60 hours.

40 The polymer obtained contains 34.1% of Br.
It is soluble in ethanol and in water-ethanol mixtures.

EXAMPLE 20. Polymer of the formula I (with R=R'=CH₃, A=(CH₂)₈, B=



45 A mixture of 130.2 g of N,N,N',N'-tetramethyl-trimethylenediamine and 264 g of p-xylidene bromide in 3,200 cm³ of anhydrous methanol is heated under reflux for 70 hours.

The polymer obtained contains 37.7% of Br.

EXAMPLE 21. Polymer of the formula I (with R=R'=CH₃, A=(CH₂)₈, B=(CH₂)₈ and X=Br)

50 A solution of 116.2 g of N,N,N',N'-tetramethyl-ethylenediamine and 216 g of 1,4-dibromobutane in 3,200 cm³ of anhydrous methanol is heated under reflux for 50 hours.

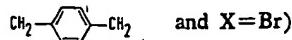
The polymer formed contains 45.8% of Br.
It is soluble in water and in water-ethanol mixtures.

EXAMPLE 22. Polymer of the formula I (with R=R'=CH₃, A=(CH₂)₆, B=(CH₂)₄ and X=Br)

A solution consisting of 130.2 g of N,N,N',N'-tetramethyl-trimethylenediamine and 216 g of 1,4-dibromobutane in 3,200 cm³ of anhydrous methanol is heated under reflux for 55 hours.

The polymer formed contains 46.2% of Br.
It is soluble in water and in ethanol.

EXAMPLE 23. Polymer of the formula I (with R=R'=CH₃, A=(CH₂)₆, B=



A mixture of 172.3 g of N,N,N',N'-tetramethyl-hexamethylenediamine and 264 g of p-xylylidene bromide in 3,200 cm³ of anhydrous methanol is heated under reflux for 1 hour.

After cooling, the precipitate is filtered off and dried. The polymer contains 34.6% of Br.
It is water-soluble.

EXAMPLE 24. Polymer of the formula I (with R=R'=CH₃, A=(CH₂)₆, B=(CH₂)₁₀ and X=Br)

A solution consisting of 172.3 g of N,N,N',N'-tetramethyl-hexamethylenediamine and 300 g of 1,10-dibromodecane in 3,200 cm³ of anhydrous methanol is heated under reflux for 15 hours.

The polymer obtained contains 32.7% of Br.
It is soluble in water and in ethanol.

EXAMPLE 25. Polymer of the formula I (with R=CH₃, R'=C₄H₉, A=(CH₂)₆, B=(CH₂)₁₀ and X=Br)

A solution of 214.4 g of N,N'-dibutyl-N,N'-dimethyl-trimethylenediamine and 300 g of 1,10-dibromodecane in 3,200 cm³ of anhydrous methanol is heated under reflux for 70 hours.

The polymer obtained contains 27.3% of Br.
It is soluble in ethanol and in water-ethanol mixtures.

EXAMPLE 26. Polymer of the formula I (with R=R'=CH₃, A=(CH₂)₆, B=(CH₂)₁₀ and X=Br)

A solution consisting of 130.2 g of N,N,N',N'-tetramethyl-trimethylenediamine and 300 g of 1,10-dibromodecane in 3,200 cm³ of anhydrous methanol is heated under reflux for 38 hours.

The polymer formed contains 34.3% of Br.
It is soluble in water and in ethanol.

EXAMPLE 27. Polymer of the formula I (with R=CH₃, R'=C₁₂H₂₅, A=(CH₂)₆, B=(CH₂)₄ and X=Br)

A solution of 480.9 g of N,N'-didodecyi-N,N'-dimethyl-hexamethylenediamine and 216 g of 1,4-dibromobutane in a mixture of 2,000 cm³ of acetonitrile and 4,000 cm³ of isopropanol is heated for 12 hours at 85° C.

The polymer formed contains 20.4% of Br.
It is soluble in ethanol.

EXAMPLE 28. Polymer of the formula I (with R=CH₃, R'=C₁₂H₂₅, A=(CH₂)₆, B=(CH₂)₄ and X=Br)

A solution of 480.9 g of N,N'-didodecyl-N,N'-dimethyl-hexamethylenediamine and 230 g of 1,5-dibromopentane in a mixture of 2,000 cm³ of acetonitrile and 4,000 cm³ of isopropanol is heated for 28 hours at 85° C.

The polymer formed contains 19.9% of Br.
It is soluble in ethanol.

On using methods analogous to those described in the preceding examples, the polymers of the formula I of which the structure is indicated in Table II below were obtained by Process 1 defined above.

TABLE II

Ex. No.	A	B	R	R'	X	Soluble in
29	(CH ₂) ₆	(CH ₂) ₆	CH ₃	CH ₃	Br	water
30	(CH ₂) ₆	(CH ₂) ₆	CH ₃	C ₁₂ H ₂₅	Br	ethanol, water-ethanol
31	(CH ₂) ₆	(CH ₂) ₁₀	CH ₃	C ₁₂ H ₂₅	Br	ethanol, water-ethanol
32	(CH ₂) ₃	(CH ₂) ₃	CH ₃	C ₁₂ H ₂₅	Br	ethanol
33	(CH ₂) ₃	(CH ₂) ₁₀	CH ₃	C ₁₂ H ₂₅	Br	ethanol
34	(CH ₂) ₁₀	(CH ₂) ₁₀	CH ₃	C ₁₂ H ₂₅	Br	ethanol
35	(CH ₂) ₆	p-xylylene	CH ₃	C ₁₂ H ₂₅	Br	ethanol
36	(CH ₂) ₆	p-xylylene	CH ₃	C ₁₂ H ₂₅	Br	ethanol
37	(CH ₂) ₆	(CH ₂) ₃	CH ₃	C ₁₂ H ₂₅	Br	ethanol, water-ethanol
38	(CH ₂) ₆	(CH ₂) ₁₁	CH ₃	C ₁₂ H ₂₅	Br	ethanol
39	(CH ₂) ₃	(CH ₂) ₁₀	CH ₃	C ₆ H ₁₃	Br	ethanol
40	(CH ₂) ₆	(CH ₂) ₁₀	CH ₃	C ₆ H ₁₃	Br	ethanol
41	(CH ₂) ₆	(CH ₂) ₃	CH ₃	cyclohexyl	Br	water-ethanol, ethanol
42	(CH ₂) ₆	(CH ₂) ₃	CH ₃	iso-C ₄ H ₉	Br	water-ethanol, ethanol
43	(CH ₂) ₆	a mixture of (CH ₂) ₁₀ , 50 mol % (CH ₂) ₃ , 50 mol %	CH ₃	CH ₃	Br	water, water-ethanol,

TABLE II (continuation)

Ex. No.	A	B	R	R'	X	Soluble in
44	(CH ₂) ₆	(CH ₂) ₆	CH ₃	iso-C ₄ H ₇	Br	water, water-ethanol
45	(CH ₂) ₆	(CH ₂) ₆	CH ₃	benzyl	Br	ethanol, water-ethanol
46	(CH ₂) ₆	(CH ₂) ₆	CH ₃	C ₄ H ₉	Br	water, water-ethanol, ethanol
47	(CH ₂) ₆ + 1.6% by weight of terminal groups -N(C ₂ H ₅) ₃	(CH ₂) ₆	CH ₃	CH ₃	Br	water, water-ethanol
48	(CH ₂) ₆ + 2.8% by weight of terminal groups -N(C ₂ H ₅) ₃	(CH ₂) ₆	CH ₃	CH ₃	Br	water, water-ethanol
49	(CH ₂) ₆ + 7.4% by weight of terminal groups -N(C ₂ H ₅) ₃	(CH ₂) ₆	CH ₃	CH ₃	Br	water, water-ethanol
50	(CH ₂) ₆	(CH ₂) ₆	CH ₃	C ₁ , ₀ H ₁₁	Br	ethanol
51	(CH ₂) ₆	p-xylylene	CH ₃	C ₁ , ₀ H ₁₁	Br	ethanol
52	p-xylylidene	(CH ₂) ₆	CH ₃	C ₄ H ₉	Br	ethanol, water-ethanol
53	(CH ₂) ₆	(CH ₂) ₆	- (CH ₂) ₆ - O - (CH ₂) ₆ -		Br	water, water-ethanol
54	(CH ₂) ₆	m-xylylidene	CH ₃	benzyl	Br	water, water-ethanol, ethanol
55	(CH ₂) ₆	(CH ₂) ₆	CH ₃	C ₄ H ₉	Br	water, water-ethanol, ethanol
56	(CH ₂) ₆	(CH ₂) ₆	CH ₃	iso-C ₄ H ₉	Br	water-ethanol ethanol

TABLE II (continuation)

Ex. No.	A	B	R	R'	X	Soluble in
57	(CH ₂) ₄	(CH ₂) ₃ (CH ₂) ₁₂	CH ₃	C ₆ H ₅	Br	water, water-ethanol
58	(CH ₂) ₆	(CH ₂) ₃	CH ₃	C ₆ H ₅	Br	water, water-ethanol, ethanol
59	(CH ₂) ₆	o-xylylene	CH ₃	C ₆ H ₅	Br	ethanol
60	(CH ₂) ₆	o-xylylene	CH ₃	CH ₃	Br	water, water-ethanol
61	(CH ₂) ₆	(CH ₂) ₃	CH ₃	CH ₃	I	water, water-ethanol
62	(CH ₂) ₁₀	(CH ₂) ₃	-(CH ₂) ₂ -O-(CH ₂) ₂ -	Br	water, water-ethanol, ethanol	
63	(CH ₂) ₆	-CH ₂ -CH ₂ -CH-	CH ₃	CH ₃	Br	water, water-ethanol
64	(CH ₂) ₁₀	(CH ₂) ₄	CH ₃	CH ₃	Br	water, water-ethanol, ethanol
65	(CH ₂) ₆	-(CH ₂) ₂ -OH	CH ₃	CH ₃	Br	water, water-ethanol, ethanol
66	-CH ₂ -CH ₂ -CH-	(CH ₂) ₆	CH ₃	C ₆ H ₅	Br	ethanol
67	(CH ₂) ₆			-(CH ₂) ₂ -O-(CH ₂) ₂ -	Br	water, water-ethanol

TABLE II (continuation)

Ex. No.	A	B	R	R'	X	Soluble in
68	(CH ₂) ₈	(CH ₂) ₈	CH ₃	CH ₃	Br	water, water-ethanol, ethanol
69	(CH ₂) ₈	(CH ₂) ₈	CH ₃	CH ₃	Br	water, water-ethanol
70	-CH ₂ -CH-(CH ₂) ₃ -CH ₂ -CH ₂ - C ₄ H ₉ C ₄ H ₉	(CH ₂) ₈	CH ₃	CH ₃	Br	ethanol
71	-CH ₂ -CH-(CH ₂) ₃ -CH ₂ -CH ₂ - C ₄ H ₉ C ₄ H ₉	(CH ₂) ₈	CH ₃	C ₄ H ₇	Br	ethanol
72	-CH ₂ -CH-CH-CH ₂ - C ₁₂ H ₂₅	(CH ₂) ₈	CH ₃	CH ₃	Br	water-ethanol, ethanol
73	-CH ₂ -CH ₂ -CH ₂ - C ₁₂ H ₂₅	(CH ₂) ₈	CH ₃	C ₄ H ₉	Br	ethanol

EXAMPLE 74. Polymer of the formula I (with R=R'=CH₃, A=B=(CH₃)₈ and X=Br)

50 g of 10-bromodecyl-dimethylamine hydrobromide, prepared according to M. R. LEHMAN, C. D. THOMPSON and C. S. MARVEL, J.A.C.S., 55, 1977 (1933) are dissolved in 200 cm³ of water. An aqueous 25% sodium hydroxide solution is added until the pH is 12. The mixture is extracted with chloroform and the extracts are evaporated to dryness. The residue is dissolved in 250 cm³ of methanol and the solution is heated under reflux for 24 hours.

10 On addition of ethyl acetate, a precipitate of the polymer formed, which contains 27.8% of Br, is obtained.

This is soluble in water and in ethanol and is practically identical with the product described above in Example 9.

The 10-bromodecyl-dimethylamine hydrobromide used as the starting material is obtained as follows: 12.6 g of 10-phenoxydecyl-dimethylamine are dissolved in 63 cm³ of a 48% strength aqueous solution of hydrobromic acid. The solution is heated to 150° C. and is distilled under atmospheric pressure until the temperature of the vapours reaches 125° C. 63 cm³ of 48% strength hydrobromic acid are added and

distillation is resumed until 110 cm³ of distillate have been obtained. The residue is evaporated to dryness under reduced pressure and the hydrobromide obtained is purified by recrystallisation from an ethanol-ether mixture.

EXAMPLE 75. Polymer of the formula I (with R=R'=CH₃, A=-(CH₂)₆, B=CH₂-CHOH-CH₂ and X=Cl). Process 1a.

A solution consisting of 172.3 g of N,N,N',N'-tetramethyl-hexamethylenediamine, 129 g of 1,3-dichloropropan-2-ol and 3,200 cm³ of acetonitrile is heated under reflux for 50 hours.

The polymer obtained contains 19.3% of Cl[⊖].

It is soluble in water and in ethanol.

EXAMPLE 76. Polymer of the formula I (with R=R'=CH₃, A=-(CH₂)₆, B=-(CH₂)₂-O-(CH₂)₂, and X=Cl). Process 1a.

A mixture of 130 g of N,N,N',N'-tetramethyl-trimethylenediamine, 143 g of 2,2'-dichloro-diethyl ether and 3,200 cm³ of dimethylformamide is heated at 100° C. for 32 hours, whilst stirring. The polymer which has precipitated is filtered off, washed with anhydrous acetone and dried.

It contains 21.5% of Cl[⊖].

It is water-soluble.

EXAMPLE 77. Polymer of the formula I (with R'=CH₃, R=—CH₂—CH₂OH, A=-(CH₂)₆, B=-(CH₂)₂, and X=Br). Process 1a.

A solution consisting of 232.3 g of N,N'-dihydroxyethyl-N,N'-dimethyl-hexamethylenediamine, 202 g of 1,3-dibromopropane and 3,200 cm³ of methanol is heated under reflux for 170 hours.

The polymer obtained contains 31.5% of Br[⊖].

It is soluble in water and in a 50:50 water-ethanol mixture.

EXAMPLE 78. Polymer of the formula I with R=R'=CH₃, A=-(CH₂)₂-S-S-(CH₂)₂,

B=-(CH₂)₆ and X=Br. Process 1a.

A mixture of 208.4 g of bis(N,N-dimethyl-2-aminoethyl)disulphide, 230 g of 1,5-dibromopentane and 3,200 cm³ of dimethylformamide is heated for 30 hours at 95° C., whilst stirring.

The polymer obtained contains 33.8% of Br[⊖].

It is soluble in water and in a 50:50 water-ethanol mixture.

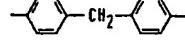
EXAMPLE 79. Polymer of the formula I (with R and R'=(CH₂)₂-O-(CH₂)₂, B=CH₂-CHOH-CH₂, A=-(CH₂)₆ and X=Br). Process 1b.

A solution consisting of 230.3 g of 1,3-dimorpholino-propan-2-ol, 244 g of 1,6-dibromohexane and 3,200 cm³ of methanol is heated under reflux for 300 hours.

The polymer obtained contains 30.0% of Br[⊖].

It is soluble in water and in a 50:50 water-ethanol mixture.

EXAMPLE 80. Polymer of the formula I (with R=R'=CH₃, A=



B=-(CH₂)₆ and X=Br. Process 1a.

A solution consisting of 254 g of N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 202 g of 1,3-dibromopropane, 900 cm³ of dimethylformamide and 900 cm³ of methanol is heated under reflux for 26 hours.

The methanol is evaporated and 2,000 cm³ of anhydrous acetone are added. The mixture is cooled and the polymer formed is filtered off. It contains 25.8% of Br[⊖]. It is soluble in water and in a 50:50 water-ethanol mixture.

EXAMPLE 81. Polymer of the formula I (with R=R'=CH₃, A=-(CH₂)₂-O-(CH₂)₂, B=—CH₂—C₆H₄—CH₂— (para), and X=Br). Process 1a.

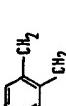
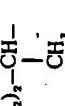
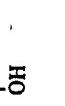
A solution consisting of 160.3 g of 2,2'-bis-(dimethylamino)-diethyl ether, 264 g of para-xylylidene bromide, 1,000 cm³ of acetonitrile and 4,000 cm³ of isopropanol is heated under reflux for 60 hours.

The polymer obtained contains 33.8% of Br⁻.
 It is soluble in water and in a 50:50 water-ethanol mixture.
 The quaternised polymers mentioned in the attached table were prepared analogously.

Ex. No.	R	R'	A	B	X	Soluble in	Process
82	CH ₃ CH ₂ OH	CH ₃	(CH ₂) ₆	(CH ₂) ₆	Br	water-water-ethanol	1a
83	"	CH ₃	"	(CH ₂) ₁₀	Br	Water	1a
84	"	C ₈ H ₁₇	"	-CH ₂ -CHOH-CH ₂ -	Br	Ethanol, water-ethanol	1a
85	"	"	"	Ph-  -CH ₂ -	Br	Ethanol	1a
86	"	C ₁₂ H ₂₅	(CH ₂) ₆	(CH ₂) ₃	Br	"	1a
87	"	CH ₃	(CH ₂) ₁₀	"	Br	Ethanol, water-ethanol	1a
88	"	CH ₃	"	(CH ₂) ₆	Br	"	1a
89	"	C ₈ H ₁₇	(CH ₂) ₆	-CH ₂ -O-(CH ₂) ₆ -	Br	Ethanol, water-ethanol	1a
90	"	CH ₃	(CH ₂) ₃	-CH ₂ -CHOH-CH ₂ -	Br	Water, Water-ethanol	1b
91	CH ₃	CH ₃	-CH ₂ -S-S-(CH ₂) ₇ -	(CH ₂) ₃	Br	Water, water-ethanol	1a
92	CH ₃	C ₈ H ₁₇	"	"	Br	Ethanol, water-ethanol	1a
93	CH ₃	CH ₃	"	(CH ₂) ₄	Br	Water, water-ethanol	1*
94	CH ₃	CH ₃	"	(CH ₂) ₆	Br	"	1a

Ex. No.	R	R'	A	B	X	Soluble in	Process
95	CH ₃	C ₁₂ H ₁₅	-(CH ₂) ₂ -S-S-(CH ₂) ₂ -	(CH ₂) ₆	Br	Ethanol, water-ethanol	1a
96	CH ₃	CH ₄	"	-CH ₂ -CHOH-CH ₂ -	Br	Water, water-ethanol	1a
97	CH ₃	CH ₃	"	(CH ₂) ₁₀	Br	"	1a
98	CH ₃	CH ₃	"	-(CH ₂) ₂ -O-(CH ₂) ₂ -	Br	"	1a
99	CH ₃	C ₂ H ₅	"	-CH ₂ -phenyl-	Br	"	1a
100	CH ₃	CH ₃	"	CH ₂ -phenyl-CH ₂	Br	"	1a
101	CH ₃	CH ₃	-(CH ₂) ₂ -S-(CH ₂) ₂ -	(CH ₂) ₃	Br	"	1a
102	CH ₃	CH ₃	-(CH ₂) ₂ -O-(CH ₂) ₂ -	-(CH ₂) ₂ -O-(CH ₂) ₂ -	Br	"	1a
103	CH ₃	CH ₃	-(CH ₂) ₂ -O-(CH ₂) ₂ -	(CH ₂) ₃	Br	"	1a
104	CH ₃	CH ₃	-(CH ₂) ₂ -O-(CH ₂) ₂ -	-(CH ₂) ₂ -CHOH-CH ₂ -	Br	"	1b
105	CH ₃	CH ₃	(CH ₂) ₃	-CH ₂ -CHOH-CH ₂ -	Br	"	1b
106	CH ₃	CH ₃	(CH ₂) ₄	-CH ₂ -CHOH-CH ₂ -	Br	Water	1b
107	CH ₃	CH ₃	(CH ₂) ₆	-CH ₂ -CHOH-CH ₂ -	Br	Water, water-ethanol	1b
108	CH ₃	CH ₃	(CH ₂) ₆	"	Br	"	1b

Ex. No.	R	R'	A	B	X	Soluble in	Process
109		$-(CH_2)_5-$	$(CH_2)_6$	$-CH_2-CHOH-CH_2$	Br	Water, ethanol	1b
110	CH ₃	CH ₃	$(CH_2)_{10}$	$-CH_2-CHOH-CH_2$	Br	Water, ethanol	1b
111	CH ₃	CH ₃		"	Br	Water, water-ethanol	1b
112	CH ₃	CH ₃	$-(CH_2)_4-S-(CH_2)_4-$	$(CH_2)_5$	Br	"	1a
113	CH ₃	CH ₃	$-(CH_2)_2-SO-(CH_2)_2-$	$(CH_2)_5$	Br	"	1a
114	CH ₃	CH ₃	$-(CH_2)_2-SO_2-(CH_2)_7-$	$(CH_2)_6$	Br	"	1a
115	CH ₃	CH ₃	$(CH_2)_6$	$-CH_2-CHOH-CH_2-$	Br	"	1a
116	CH ₃	C ₄ H ₉	$(CH_2)_6$	$-CH_2-CHOH-CH_2-$	Br	Water, ethanol	1a
117	CH ₃	C ₄ H ₉		$-(CH_2)_4-O-(CH_2)_4-$	Br	Water, water-ethanol	1a
118	CH ₃	C ₁₂ H ₂₅	$(CH_2)_5$	"	Br	Ethanol	1a
119	CH ₃	CH ₃	$(CH_2)_6$	"	Cl	Water, water-ethanol	1a
120	CH ₃	C ₆ H ₁₃	$(CH_2)_6$	"	Br	Ethanol, water-ethanol	1a
121	CH ₃	CH ₃	$(CH_2)_4$	$(CH_2)_7$	Br	Water, ethanol	1a
122	CH ₃	CH ₃	$(CH_2)_4$	$(CH_2)_6$	Br	"	1a

Ex. No.	R	R'	A	B	X ₂	Soluble in	Process
123	CH ₃	CH ₃	(CH ₃) ₄		Br	Water	1a
124	CH ₃	CH ₃	(CH ₃) ₃		Br	Water, ethanol	1a
125	CH ₃	CH ₃	(CH ₃) ₂ -O-(CH ₂) ₂		Br	Water	1a
126	CH ₃	CH ₃			Br	Alcohol	1a
127	CH ₃	CH ₃			Br	Water, ethanol	1a
128	-(CH ₂) ₃	-(CH ₂) ₃			Br	Water	1b
129	-(CH ₂) ₃	-(CH ₂) ₃			Br	Water	1b

Ex. No.	R	R'	A	B	X	Soluble in	Process
130	CH ₃	iso C ₄ H ₉	(CH ₃) ₃	(CH ₃) ₂ (CH ₃) ₂	Br	Water, ethanol	1a
131	CH ₃	iso C ₄ H ₉	(CH ₃) ₃	Br	Water	1a	
132	CH ₃	C ₃ H ₇	(CH ₃) ₆	-(CH ₃) ₂ -CH- CH ₃	Br	Water	1a
133	CH ₃	C ₃ H ₇	(CH ₃) ₆		Br	Water, ethanol	1a
134	CH ₃	benzyl	(CH ₃) ₆	CH ₃ -CH-CH ₂ OH	Br	Water, ethanol	1a
135	CH ₃	,	(CH ₃) ₆	-CH ₃ -CH-CH ₂ OH	Cl	Ethanol	1a
136	CH ₃	C ₄ H ₉			Br	Water	1a
137	CH ₃	CH ₃			Br	Water, ethanol	1a

Ex. No.	R	R'	A	B	X	Soluble in	Process
138	CH ₃	C ₂ H ₅		(CH ₂) ₁₀	Br	Water, ethanol	1a
139	CH ₃	C ₂ H ₅	(CH ₂) ₃	(CH ₂) ₄	Br	"	1a
140	CH ₃	C ₂ H ₅	(CH ₂) ₆	(CH ₂) ₄	Br	"	1a

EXAMPLES OF COSMETIC COMPOSITIONS AND OF COSMETIC TREATMENT

EXAMPLE I. Hand treatment creams.

5. 1. The following cream is prepared:

	"Vaseline" oil	10	g
	Cetyl alcohol	6	g
	Self-emulsifiable glyceryl monostearate	4	g
	Triethanolamine	2	g
10	Methyl p-hydroxybenzoate	0.1	g
	Polymer of Example 1	4	g
	Water, q.s.p.	100	g

This cream is applied to the hands, whilst rubbing them to cause the cream to penetrate.

15. The hands are soft and pleasant to the touch.

2. Analogous results are obtained by replacing the 4 grams of polymer of Example 1 in the above cream formulation by 3.5 grams of polymer of Example 15.

EXAMPLE II. Carrier creams for dyeing (oxidation dyeing).

1. A cream of the following formulation is prepared:

	Cetyl/stearyl alcohol	20	g	
5	Oleyl diethanolamide	4	g	5
	Sodium cetyl/stearyl-sulphate	3	g	
	Polymer of Example 15	5	g	
	Ammonia, 22°B strength (11N)	10	ml	
	m-Diaminoanisole sulphate	0.048	g	
10	Resorcinol	0.420	g	10
	m-Aminophenol base	0.150	g	
	Nitro-p-phenylenediamine	0.085	g	
	p-Toluylenediamine	0.004	g	
	Triton B ②	1	g	
15	Sodium bisulphite, d=1.32	1,200	g	15
	Water, q.s.p.	100	g	

② "Triton" B: the tetrasodium salt of ethylenediaminetetra-acetic acid. ["Triton" is a Registered Trade Mark.]

30 g of this cream are mixed with 45 g of hydrogen peroxide of 20 volumes strength. A smooth thick cream which is pleasant to apply and adheres well to the hair is obtained.

After waiting for 30 minutes, the hair is rinsed and dried.

On 100% white hair, a blond shade is obtained. The hair is easy to comb out whether wet or dry. The hair looks shiny and is pleasant and silky to the touch.

2. A cream of the following formulation is prepared:

25	Cetyl/stearyl alcohol	20	g	25
	Oleyl diethanolamide	4	g	
	Sodium cetyl/stearyl-sulphate	3	g	
	Polymer of Example 3	5	g	
	Ammonia, 22°Be strength (11N)	12	ml	
30	m-Diaminoanisole sulphate	0.048	g	30
	Resorcinol	0.420	g	
	m-Aminophenol base	0.150	g	
	Nitro-p-phenylenediamine	0.085	g	
	p-Toluylenediamine	0.004	g	
35	Triton B	1	g	35
	Sodium bisulphite, d=1.32	1,200	g	
	Water, q.s.p.	100	g	

30 g of this cream are mixed with 45 g of hydrogen peroxide of 20 volumes strength. A smooth thick cream which is pleasant to apply and adheres well to the hair is obtained.

After waiting for 30 minutes, the hair is rinsed and dried.

On 100% white hair, a blond shade is obtained. The hair is easy to comb out either wet or dry. The hair looks shiny and is pleasant and silky to the touch.

EXAMPLE III. Wavesetting lotion for sensitised hair.

1. An alcoholic lotion of the following formulation is prepared:

	Polyvinylpyrrolidone	1	g	
	Polymer of Example 7	1	g	
	Ethyl alcohol, q.s.p.	100	ml	

This solution is applied to the hair, the hair is set in waves and is dried.

The hair is strengthened and plasticised.

The hair is shiny and bulky; it is silky to the touch and easy to comb out.

2. Analogous results are obtained on replacing the polymer of Example 7 in the above formulation by the polymer of Example 16.

3. The lotion of the following formulation is prepared:

55	Polymer of Example 18	0.8	g	55
	Polyvinylpyrrolidone/vinyl acetate, 60:40	1.0	g	
	Triethanolamine, q.s. pH 6			
	Water, q.s.p.	100	ml	

The lotion is applied to bleached hair. The hair is set in waves and dried.
Analogous results to those of the preceding example are obtained.

4. The lotion of the following formulation is prepared:

5	Polymer of Example 19 Polyvinylpyrrolidone/vinyl acetate, 60:40 copolymer Ethyl alcohol, q.s. 50° Triethanolamine, q.s. pH 7 Water, q.s.p.	1 g 1 g 100 ml	5
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10 The lotion is applied to bleached hair. The hair is set in waves and dried.
Analogous results to those of the preceding example are obtained.

5. The lotion of the following formulation is prepared:

15	Polymer of Example 17 Vinyl acetate/crotonic acid, 90:10 copolymer Triethanolamine, q.s. pH 7.5 Water, q.s.p.	1.5 g 1.5 g 100 ml	15
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The lotion is applied to bleached hair. The hair is set in waves and dried.
Analogous results to those of the preceding example are obtained.

8. The following solution is prepared:

20	Polymer of Example 2 Vinyl acetate/crotonic acid, 90:10 copolymer Monoethanolamine, q.s. pH 7 Water, q.s.p.	1.5 g 1.5 g 100 ml	20
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The solution is applied to bleached hair. The hair is set in waves and dried.
Analogous results to those of the preceding example are obtained.

25 EXAMPLE IV—Treatment lotions (application with rinsing)
1. 30 ml of the following solution are applied to clean, wet hair:

30	Polymer of Example 20 Monoethanolamine, q.s. pH 7.5 Water, q.s.p.	5 g 100 ml	30
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The lotion is allowed to act for 5 minutes and the hair is then rinsed.
The hair is soft to the touch and easy to comb out.
It is set in waves and dried.

The dry hair is easy to comb out.
The hair is shiny and springy, and has body.

35 2. 25 ml of the following solution are applied to clean, wet hair:

40	Polymer of Example 12 Citric acid, q.s. pH 6 Water, q.s.p.	6 g 100 ml	40
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The lotion is allowed to act for 5 minutes and the hair is then rinsed.
The hair is soft to the touch and easy to comb out.
It is set in waves and dried.
The dry hair is easy to comb out.
The hair is shiny and springy, and has body.

3. 25 ml of the following solution are applied to clean, wet hair:

45	Polymer of Example 21 Triethanolamine, q.s. pH 6 Water, q.s.p.	6 g 100 ml	45
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The lotion is allowed to act for 5 minutes and the hair is then rinsed.
The hair is soft to the touch and easy to comb out.
It is set in waves and dried.
The dry hair is easy to comb out.

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The hair is shiny and springy, and has body.
4. 30 ml of the following solution are applied to clean, wet hair:

	Polymer of Example 22 Water, q.s.p.	7 g 100 ml	
5	The pH is about 7.		5
	The lotion is allowed to act for 5 minutes and the hair is then rinsed. The hair is soft to the touch and easy to comb out. It is set in waves and dried. The dry hair is easy to comb out.		
10	The hair is shiny and springy, and has body.		10
	5. 25 ml of the following solution are applied to clean, wet hair:		
	Polymer of Example 23 Monooethanolamine, q.s. pH 5 Water, q.s.p.	5 g 100 ml	
15	The lotion is allowed to act for 5 minutes and the hair is then rinsed. The hair is soft to the touch and easy to comb out. It is set in waves and dried. The dry hair is easy to comb out. The hair is shiny and springy, and has body.		15
20	EXAMPLE V.—Structuring lotion (applied without rinsing). 1. Prior to use, 0.3 g of N,N'-di-hydroxymethylmethylenethiourea, hereafter referred to as compound A, is mixed with 25 ml of a solution containing:		20
25	Polymer of Example 11 Hydrochloric acid, q.s. pH 2.7 Water, q.s.p.	0.4 g 100 ml	25
	The mixture is applied to hair which has been washed and towelled dry before setting it in waves. The hair can be combed out easily and is silky to the touch. It is set in waves and dried.		
30	The hair is shiny and springy; it has body (bulk), is silky to the touch and is easy to comb out.		30
	2. Prior to use, 0.4 g of compound A is mixed with 25 ml of a solution containing:		
35	Polymer of Example 14 Phosphoric acid, q.s. pH 2.7 Water, q.s.p.	0.5 g 100 ml	35
	The mixture is applied to hair which has been washed and towelled dry before setting it in waves. The hair can be combed out easily and is silky to the touch. It is set in waves and dried.		
40	The hair is shiny and springy; it has body (bulk), is silky to the touch and is easy to comb out.		40
	3. Prior to use, 0.5 g of compound A is mixed with 25 ml of a solution containing:		
45	Polymer of Example 24 Phosphoric acid, q.s. pH 3 Water, q.s.p.	0.6 g 100 ml	45
	The mixture is applied to hair which has been washed and towelled dry before setting it in waves. The hair can be combed out easily and is silky to the touch. It is set in waves and dried.		
50	The hair is shiny and springy; it has body (bulk), is silky to the touch and is easy to comb out.		50

4. Prior to use, 0.6 g of compound A is mixed with 25 ml of a solution containing:

Polymer of Example 13	0.7 g
Hydrochloric acid, q.s. pH 3	
Water, q.s.p.	100 ml

5 The mixture is applied to hair which has been washed and towelled dry before setting it in waves. 5

The hair can be combed out easily and is silky to the touch.

It is set in waves and dried.

10 The hair is shiny and springy; it has body (bulk), is silky to the touch and is easy to comb out. 10

5. Prior to use, 0.5 g of compound A is mixed with 25 ml of a solution containing:

Polymer of Example 1	0.5 g
Phosphoric acid, q.s. pH 3	
Water, q.s.p.	100 ml

15 The mixture is applied to hair which has been washed and towelled dry before setting it in waves.

The hair can be combed out easily and is silky to the touch.

It is set in waves and dried.

20 The hair is shiny and springy; it has body (bulk), is silky to the touch and is easy to comb out. 20

EXAMPLE VI—Structuring lotion (application with rinsing).

1. Prior to use, 2 g of compound A are mixed with 25 ml of a solution containing:

Polymer of Example 25	5 g
Hydrochloric acid, q.s. pH 2.5	
Water, q.s.p.	100 ml

25 The mixture is applied to hair which has been washed and towelled dry. It is left to act for 10 minutes, and the hair is rinsed.

30 The hair can be combed out easily and is soft (silky) to the touch.

It is set in waves and dried under a hood.

The dry hair can be combed out easily.

It is shiny and springy and has body (bulk).

35 2. Prior to use, 1.8 g of compound A are mixed with 25 ml of a solution containing: 35

Polymer of Example 26	6 g
Phosphoric acid, q.s. pH 3	
Water, q.s.p.	100 ml

40 The mixture is applied to hair which has been washed and towelled dry. It is left to act for 10 minutes, and the hair is rinsed.

The hair can be combed out easily and is soft (silky) to the touch.

It is set in waves and dried under a hood.

The dry hair can be combed out easily.

It is shiny and springy and has body (bulk).

45 3. Prior to use, 1.5 g of compound A are mixed with 25 ml of a solution containing: 45

Polymer of Example 13	4 g
Hydrochloric acid, q.s. pH 3	
Water, q.s.p.	100 ml

50 The mixture is applied to hair which has been washed and towelled dry. It is left to act for 10 minutes, and the hair is rinsed.

The hair can be combed out easily and is soft (silky) to the touch.

It is set in waves and dried under a hood.

The dry hair can be combed out easily.

55 It is shiny and springy and has body (bulk). 55

4. Prior to use, 2 g of compound A are mixed with 25 ml of a solution containing:

5	Polymer of Example 1 Phosphoric acid, q.s. pH 2.8 Water, q.s.p.	5 g 100 ml	5
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The mixture is applied to hair which has been washed and towelled dry.
It is left to act for 10 minutes, and the hair is rinsed.

The hair can be combed out easily and is soft (silky) to the touch.

It is set in waves and dried under a hood.

The dry hair can be combed out easily.

It is shiny and springy and has body (bulk).

5. Prior to use, 1.5 g of compound A are mixed with 25 ml of a solution containing:

15	Polymer of Example 11 Phosphoric acid, q.s. pH 3 Water, q.s.p.	5.5 g 100 ml	15
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The mixture is applied to hair which has been washed and towelled dry.
It is left to act for 10 minutes, and the hair is rinsed.

The hair can be combed out easily and is soft (silky) to the touch.

It is set in waves and dried under a hood.

The dry hair can be combed out easily.

It is shiny and springy and has body (bulk).

EXAMPLE VII—Shampoos.

1. The following solution is prepared:

25	C ₁₁ —C ₁₄ α-diol condensed with 3 to 4 molecules of glycidol Polymer of Example 1 Lactic acid, q.s.p. Water, q.s.p.	17 g 3 g pH 3.5 100 cm ³	25
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30 When applied to the head, this solution, which has a limpid appearance, produces a copious and rather soft foam and assists the combing out of the wet hair. After drying, the hair is springy, light and shiny. 30

2. The following solution is prepared:

35	C ₁₂ H ₂₅ —(O—CH ₂ —CHOH—CH ₂) ₄ OH (lauryl alcohol condensed with 4 molecules of glycidol or epichlorohydrin) Polymer of Example 1 Tertiary stearylamine polyoxyethylenated with 5 mols of ethylene oxide Lactic acid, q.s.p. Water, q.s.p.	15 g 2 g 1.5 g pH 4.5 100 cm ³	35 40
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45 When applied to the head, this solution, of limpid appearance, produces a copious and soft foam which is readily removed by rinsing. The hair is very easy to comb out and after drying possesses bulk and springiness whilst remaining soft and easy to style. 45

3. The following solution is prepared:

50	C ₁₁ —C ₁₄ α-diol condensed with 3 to 4 molecules of glycidol Polymer of Example 12 Lactic acid, q.s.p. Water, q.s.p.	17 g 3 g pH 3.5 100 cm ³	50
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When applied to the head, this solution, of limpid appearance, produces a copious and rather soft foam and makes it possible to improve the combing out of the wet hair. After drying, the hair is soft and shiny and has a lightweight appearance.

EXAMPLE VIII.—Anti-dandruff lotions which assist combing out.

1. The following solution is prepared:

5	Magnesium bis-(2-pyridyl-1-oxide)-disulphide, sold under the tradename "Omadine MDS" (Olin Mathieson) ["Omadine" is a Registered Trade Mark]	0.5 g	5
10	Polymer of Example 1 Polyvinylpyrrolidone (sic)/vinyl acetate, 70:30 copolymer	0.7 g	
	KOH, q.s.p.	pH 5.5	10
	Water, q.s.p.	100 cm ³	

When applied to the head of hair, this lotion not only has an anti-dandruff action but facilitates the combing out of the hair.

2. The following lotion is prepared:

15	4-Ethylbenzyl-alkyl-dimethyl-ammonium chloride, in which the alkyl group is a mixture of C ₁₂ —C ₁₄ and C ₁₄ —C ₁₈	1 g	15
20	Polymer of Example 1 Polyvinylpyrrolidone/vinyl acetate, 70:30 copolymer	0.7 g	
	KOH, q.s.p.	pH 5.5	20
	Water, q.s.p.	100 cm ³	

The application of this lotion, which causes a considerable reduction in dandruff after a few weeks, permits easy combing out of the hair.

EXAMPLE IX.—Anti-seborrhoeic lotion (for daily use), which assists combing out.

The following solution is prepared:

25	Carboxymethyl-cystein	0.3 g	25
	Polymer of Example 7	0.2 g	
	Cationic polyglucoside derivative sold by National Starch under the name "781568"	0.3 g	
30	Ethyl alcohol	50°	30
	KOH, q.s.p.	pH 7	
	Water, q.s.p.	100 cm ³	

When applied daily to greasy hair, this lotion improves the appearance of the head of hair, which becomes easy to style and to comb out.

EXAMPLE X.—DYEING CARRIER CREAM (oxidation dyeing).

1. A cream of the following formulation is prepared:

35	Cetyl/stearyl alcohol	22 g	35
	Oleyl-diethanolamide	5 g	
40	Sodium cetyl/stearyl-sulphate	4 g	
	Compound of Example 105	6 g	40
	Ammonia, 11 N	12 cm ³	
	m-Diaminoanisole sulphate	0.048 g	
45	Resorcinol	0.420 g	
	m-Aminophenol base	0.150 g	
	Nitro-p-phenylenediamine	0.085 g	45
	p-Toluylenediamine	0.004 g	
	"Tilon" B*	1.000 g	
50	Sodium bisulphite (d=1.32)	1.200 g	
	Water, q.s.p.	100 g	
	*"Tilon" B: tetrasodium salt of ethylenediaminetetraacetic acid.		50

30 g of this formulation are mixed with 45 g of hydrogen peroxide of 20 volumes strength. A smooth, thick cream is obtained, which is pleasant to apply and which adheres well to the hair.

After waiting for 30 minutes, the hair is rinsed and dried.

On 100% white hair, a blond shade is obtained. The hair is easy to comb out

55

either wet or dry. The hair has a shiny appearance and is pleasant and silky to the touch.

The same result is obtained on replacing the compound of Example 105 by one of the compounds of the following examples:

5	Example 106	5%	5
	Example 107	5%	
	Example 108	6%	
	Example 110	4.5%	
10	Example 111	6%	10
	Example 76	3%	

2. A cream of the following formulation is prepared:

15	Stearyl alcohol	18	g
	Coconut monoethanolamide	6	g
	Ammonium lauryl-sulphate (20% of fatty alcohol)	10	g
	Compound of Example 119	4	g
20	Ammonia, 22° Bé strength (11 N)	10	cm ³
	m-Diaminoanisole sulphate	0.048	g
	Resorcinol	0.420	g
	m-Aminophenol base	0.150	g
	Nitro p-phenylenediamine	0.085	g
	p-Toluylenediamine	0.004	g
	Trilon B	1.000	g
	Sodium bisulphite (d=1.32)	1.200	g
	Water, q.s.p.	100	g

25 30 g of this formulation are mixed with 45 g of hydrogen peroxide of 20 volumes strength. A smooth, thick cream is obtained, which is pleasant to apply and which adheres well to the hair.

After waiting for 30 minutes, the hair is rinsed and dried.

On 100% white hair, a blond shade is obtained. The hair is easy to comb out either wet or dry. The hair has a shiny appearance and is pleasant and silky to the touch.

The same result is obtained on replacing the compound of Example 119 by one of the compounds of the following examples:

35	Example 75	5%	35
	Example 104	4%	
	Example 102	5%	
	Example 81	5.5%	
	Example 103	6%	

EXAMPLE XI.—DYEING SHAMPOOS.

40 1. A dyeing shampoo of the following formulation is prepared: 40

45	Nonylphenol+4 mols of ethylene oxide	25	g
	Nonylphenol+9 mols of ethylene oxide	23	g
	Compound of Example 89	4	g
	Ethyl alcohol, 96% strength	7	g
50	Propylene glycol	14	g
	Ammonia, 22 Bé strength (11 N)	10	cm ³
	m-Diaminoanisole sulphate	0.030	g
	Resorcinol	0.400	g
	m-Aminophenol base	0.150	g
	p-Aminophenol base	0.087	g
	Nitro p-phenylenediamine	1.000	g
	Trilon B	3.000	g
	Sodium bisulphite (d=1.32)	1.200	g
	Water, q.s.p.	100	g

55 50 g of this formulation are mixed with the same quantity of hydrogen peroxide of 20 volumes strength and the gel obtained is applied to hair by means of a brush. The mixture is left for 30 minutes and the hair is then rinsed. 55

The hair is easy to brush out and is silky to the touch. It is set in waves and dried.

The hair is shiny and springy and has body (bulk); it is silky to the touch and easy to comb out.

5 A chestnut tint is obtained on a brown background. 5

2. A dyeing shampoo of the following formulation is prepared:

	Nonylphenol + 4 mols of ethylene oxide	25	g
	Nonylphenol + 9 mols of ethylene oxide	23	g
10	Compound of Example 118	5	g
	Ethyl alcohol, 96% strength	7	g
	Propylene glycol	14	g
	Ammonia, 22 Bé strength (11 N)	10	cm ³
	m-Diaminoanisole sulphate	0.030	g
15	Resorcinol	0.400	g
	m-Aminophenol base	0.150	g
	p-Aminophenol base	0.087	g
	Nitro p-phenylenediamine	1.000	g
	Triton B	3.000	g
	Sodium bisulphite (d=1.32)	1.200	g
20	Water, q.s.p.	100	g

50 g of this formulation are mixed with the same quantity of hydrogen peroxide of 20 volumes strength and the gel obtained is applied to hair by means of a brush.

The mixture is left for 30 minutes and the hair is then rinsed.

25 The hair is easy to brush out and is silky to the touch. It is set in waves and dried. 25

The hair is shiny and springy and has body (bulk); it is silky to the touch and easy to comb out.

A chestnut tint is obtained on a brown background.

30 EXAMPLE XII.—TREATMENT LOTION (*application with rinsing*). 30
30 ml of the following solution are applied to clean, wet hair:

Compound of Example 94	5	g
Monoethanolamine, q.s.	pH 7.5	
Water, q.s.p.	100	cm ³

35 After waiting for 5 minutes, the hair is rinsed. 35
The hair is soft to the touch and can be combed out easily.

It is set in waves and dried.

The dry hair can be combed out easily. It is shiny and springy and has body.

The same result is obtained by replacing the compound of Example 94 by one of the compounds of the following examples:

40	Example 91	4	g
	Example 78	6	g
	Example 93	6	g
	Example 100	4	g
	Example 97	6	g
45	Example 112	5	g
	Example 96	5	g
	Example 98	6.5	g
	Example 101	4.5	g
	Example 99	5	g

50 EXAMPLE XIII.—STRUCTURING LOTION (*application with rinsing*). 50
1. Prior to use, 2 g of N,N'-di-hydroxymethylmethylenethiourea are mixed with 25 cm³ of a solution containing:

55	Compound of Example 117	5	g
	Hydrochloric acid, q.s.	pH 2.5	
	Water, q.s.p.	100	cm ³

The mixture is applied to hair which has been washed and towelled dry.

After waiting for 10 minutes the hair is rinsed.
 The hair is easy to comb out and is soft (silky) to the touch.
 It is set in waves and dried under a hood.
 The dry hair can be combed out easily, is shiny and springy and has body
 (bulk).
 2. Prior to use, 2 g of N,N'-di-hydroxymethylethylenethiourea are mixed with
 25 cm³ of a solution containing:

10	Compound of Example 79 Hydrochloric acid, q.s. Water, q.s.p.	pH 2.5 100 cm ³	3 g 10
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The mixture is applied to hair which has been washed and towelled dry.
 After waiting for 10 minutes the hair is rinsed.
 The hair is easy to comb out and is soft (silky) to the touch.
 It is set in waves and dried under a hood.
 The dry hair can be combed out easily, is shiny and springy and has body
 (bulk).
 3. Prior to use, 2 g of N,N'-di-hydroxymethylethylenethiourea are mixed with
 25 cm³ of a solution containing:

20	Compound of Example 109 Hydrochloric acid, q.s. Water, q.s.p.	pH 2.5 100 cm ³	4 g 20
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The mixture is applied to hair which has been washed and towelled dry.
 After waiting for 10 minutes the hair is rinsed.
 The hair is easy to comb out and is soft (silky) to the touch.
 It is set in waves and dried under a hood.
 The dry hair can be combed out easily, is shiny and springy and has body
 (bulk).

EXAMPLE XIV.—STRUCTURING LOTION (application without rinsing).
 Prior to use, 0.3 g of N,N'-di-hydroxymethylethylenethiourea is mixed with 25
 cm³ of a solution containing:

	Compound of Example 82 Phosphoric acid, q.s. Water, q.s.p.	pH 2.8 100 cm ³	0.5 g
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The mixture is applied to hair which has been washed and dried, before setting
 it in waves.
 The hair is easy to comb out and is silky to the touch.
 It is set in waves and dried.
 The hair is shiny and springy, it has body (bulk), is silky to the touch and is
 easy to comb out.
 The same result is obtained on replacing the compound of Example 82 by one of
 the compounds of the following examples:

45	Example 77 0.4 g Example 87 0.6 g Example 83 0.4 g Example 88 0.5 g	1 g 2.5 g 100 cm ³	35 40 45
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EXAMPLE XV.—WAVESETTING LOTION FOR SENSITISED HAIR.
 1. A wavescetting lotion of the following formulation is prepared:

50	Polyvinylpyrrolidone Compound of Example 92 Ethyl alcohol, q.s.	1 g 2.5 g 100 cm ³	50
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The solution is applied to the hair. The hair is set in waves and dried.
 The hair is strengthened and plasticised.
 It is shiny and bulky; it is silky to the touch and easy to comb out.

The same result is obtained on replacing the compound of Example 92 by the following product:

Compound of Example 120 2%

2. A wavesetting lotion of the following formulation is prepared:

5	Polyvinylpyrrolidone	1 g	5
	Compound of example 85	1 g	
	Ethyl alcohol, q.s.	100 cm ³	

The solution is applied to the hair. The hair is set in waves and dried.
The hair is hardened and plasticised.

10	It is shiny and bulky; it is silky to the touch and easy to comb out.	10
	The same result is obtained on replacing the compound of Example 85 by the following product:	

Compound of Example 84 1.2 g

3. A wavesetting lotion of the following formulation is prepared:

15	Polyvinylpyrrolidone	1 g	15
	Compound of Example 86	0.8 g	
	Ethyl alcohol, q.s.	100 cm ³	

20	The solution is applied to the hair. The hair is set in waves and dried. The hair is hardened and plasticised.	20
	It is shiny and bulky; it is silky to the touch and easy to comb-out.	

EXAMPLE XVI.—PRE-SHAMPOOING COMPOSITION.

10 g of the following solution is applied to dirty, dry hair:

25	Compound of Example 1 Monoethanolamine q.s.p. Water, q.s.p.	2 g pH 7 100 cm ³	25
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After waiting for two minutes, the hair is given a conventional two-stage anionic shampoo.

30	The wet hair is easy to comb out and the hair is soft. After setting in waves and drying, the hair combs out easily and is soft to the touch.	30
	The hair is shiny and springy. The same solution can be packaged as an aerosol.	

EXAMPLE XVII.—PRE-SHAMPOOING COMPOSITION.

15 g of the following solution is applied to dirty, dry hair:

35	Compound of Example 13 Compound of Example 17 Monoethanolamine q.s.p. Water, q.s.p.	1 g 1 g pH 7 100 cm ³	35
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40	After waiting for two minutes, the hair is given a conventional two-stage anionic shampoo. The wet hair is easy to comb out and the hair is soft. After setting in waves and drying, the hair combs out easily and is soft to the touch.	40
45	The hair is shiny and springy. The same solution can be packaged as an aerosol with nitrogen or nitrous oxide or freons as propellants.	45

EXAMPLE XVIII.—TREATMENT LOTION FOR USE BEFORE DYEING.
20 cm³ of the following solution are applied to dry, dirty hair:

After waiting for 5 minutes, a conventional ammoniacal oxidation dye is applied. It is left for 30 minutes.

After rinsing and giving an anionic shampoo, the hair combs out very easily.
After wavesetting and drying, the hair is silky, shiny, springy and easy to style.

10 EXAMPLE XIX.—ANIONIC SHAMPOO. 10

Triethanolamine lauryl-sulphate	10	g
Compound of Example 17	1	g
Triethanolamine, q.s.p.	pH 8	
Water, q.s.p.	100	g

EXAMPLE XX.—PRE-SHAMPOOING COMPOSITION.

Compound of Example 17 2 g
Monoethanolamine, q.s.p. pH 7
Water, q.s.p. 100 g

10 g of this composition are applied to dry, dirty hair.

After waiting for 2 minutes, the hair is given a conventional anionic shampoo.

The hair is easy to comb out and is soft to the touch both when wet and after drying.

Analogous results are obtained on replacing the compound of Example 17 by the compounds of Examples 1, 7, 13, 20, 22, 23, 46, 75, 76, 91, 92, 93, 105, 108, 110, 111, 112, 117, 123, 130, 136 or 140.

Analogous pre-shampooing compositions were prepared in the form of aerosol packs, using the same compounds. For example, the following procedure can be followed:

The following solution is prepared:

30 Compound of Example 17 8 g
 Monoethanolamine, q.s.p. pH 7
 Water, q.s.p. 100 g

25 g of this solution are introduced into an aerosol container and nitrogen is then introduced until the pressure reaches 12 kg/cm².

35 Dry hair which is to be washed is impregnated using the aerosol pack thus obtained and after waiting for a few minutes the hair is given a conventional anionic shampoo.

EXAMPLE XXI.—PRE-SHAMPOOING COMPOSITION IN THE FORM OF AN AEROSOL FOAM.

40 The following formulation is prepared as an aerosol: 40

45	Na cetyl/stearyl-sulphate	1.3 g
	Nonylphenol ethoxylated with 4 mols of ethylene oxide	2.5 g
	Nonylphenol ethoxylated with 9 mols of ethylene oxide	1.5 g
	Compound of Example 17	3.0 g
	Water	81.7 g
	"Freon" 114—"Freon" 12 mixture (70:30)	10.0 g
	Degree of filling 65%.	

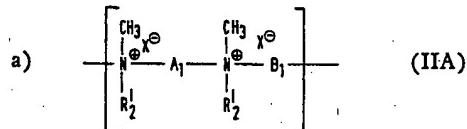
The foam is applied to dirty, dry hair whilst rubbing so as to cause the product to penetrate thoroughly into the hair.

A conventional anionic shampoo is applied.

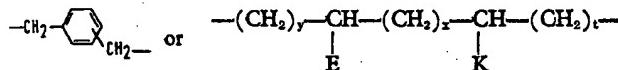
After waiting for 2 to 3 minutes, the hair is rinsed. The hair is soft to the touch and is easy to comb out.

The hair is set in waves and dried. The dry hair combs out easily. It is shiny and springy and has body (bulk).

It should be noted that some of the polymers used in the present invention are described and claimed in our Application No. 20683/75 (Serial No. 1,513,671), which provides a quaternised polymer having recurring units of the formula:

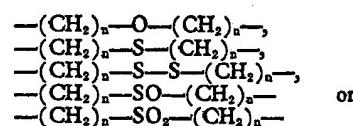


5 in which each A_1 radical, which may be the same or different, represents either A, A being a group of the formula:

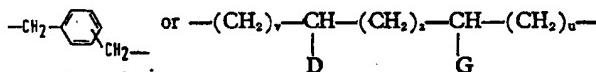


in which x, y and t each independently is 0 or an integer from 1 to 11, and E and K each independently is a hydrogen atom or an aliphatic radical, such that the radical contains less than 18 carbon atoms, or

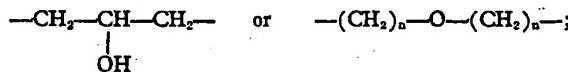
10 radical contains less than 18 carbon atoms,
A represents a group of the formula:



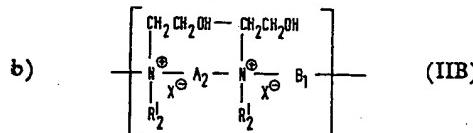
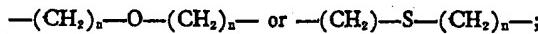
in which n is 2 or 3; X^\ominus is an anion derived from an inorganic or organic acid; R'_2 is an alkyl, alicyclic or arylaliphatic radical containing at most 20 carbon atoms; each B_1 radical, which may be the same or different, represents either B, B being a group of the formula:



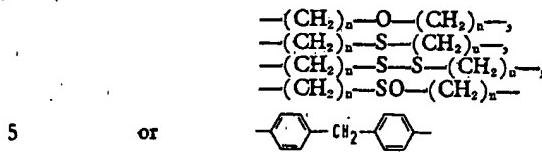
in which D and G each independently is a hydrogen atom or an aliphatic radical, and v, z and u each independently is 0 or an integer from 1 to 11, such that up to two of them can be 0 and such that the radical contains less than 18 carbon atoms and the sum $(v+z+u)$ is greater than 1 when the sum $(x+y+r)$ is equal to zero, or B₁ represents a group of the formula:



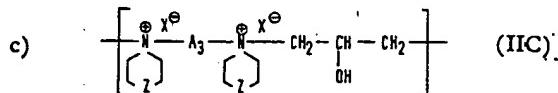
with the proviso that R'_2 has at least 3 carbon atoms when A_1 or B_1 represents $-(CH_2)_n-O-(CH_2)_m-$, or when, simultaneously, $A_1=A$ and $B_1=B$ and that R'_2 does not represent a methyl radical when $A_1=A$ or A_1 represents



in which each A_2 radical, which may be the same or different, represents either A as defined above, or a group of the formula:

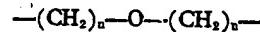


n, X, R'₂ and B₁ being defined as above; or



in which Z represents an oxygen atom or the —CH₂— group; each A₁ radical, which may be the same or different, represents either A as defined above, or

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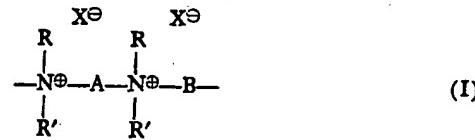
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and X and n are as defined above as well as compositions containing such a polymer and a method of treating the skin or hair with it. No claim is made herein to the use of these polymers.

15

Subject to this disclaimer: WHAT WE CLAIM IS:—

1. A method of treating the hair and/or skin which comprises applying thereto at least one quaternised polymer possessing recurring units of the general formula:



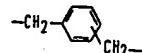
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in which: each R radical, which may be the same or different, is a C₁ to C₅ alkyl group or a —CH₂—CH₂OH group, each R' radical, which may be the same or different, is an aliphatic radical, an alicyclic radical or an araliphatic radical, which radical contains at most 20 carbon atoms, or R and R' attached to the same nitrogen atom form, with the latter, a ring which can contain a second hetero-atom other than nitrogen, each A radical, which may be the same or different, represents a divalent group having one of the formulae:

20

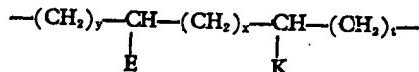
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(i)



25

(ii)



in which x, y and t are each independently 0 or an integer from 1 to 11 such that the sum (x+y+t) is 0 to 17, and E and K are each independently a hydrogen atom or an aliphatic radical having fewer than 18 carbon atoms,

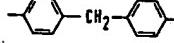
30

- (iii) —(CH₂)_n—S—(CH₂)_n—
- (iv) —(CH₂)_n—O—(CH₂)_n—
- (v) —(CH₂)_n—S—S—(CH₂)_n—
- (vi) —(CH₂)_n—SO—(CH₂)_n—
- (vii) —(CH₂)_n—SO₂—(CH₂)_n—

30

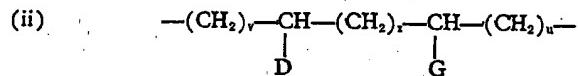
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or (viii)

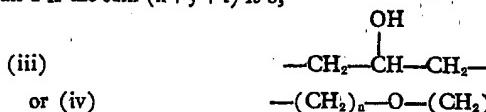


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in which n is 2 or 3, each B radical, which may be the same or different, represents a divalent group having one of the formulae:

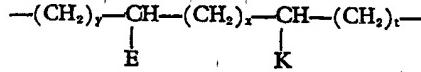


in which D and G each independently are a hydrogen atom or an aliphatic radical having less than 18 carbon atoms, and v, z and u are each independently 0 or an integer from 1 to 11, and any two of them can simultaneously be 0, such that the sum (v+z+u) is at least 1 but not greater than 17 and the sum (v+z+u) is greater than 1 if the sum (x+y+t) is 0,

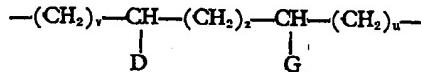


n being defined as above, and X^\ominus represents an anion derived from an organic or inorganic acid.

2. A method according to claim 1, in which A represents an o-, m- or p-xylylene group or a group of the formula:



15 in which E, K, x, y and t are defined as in claim 1, and B represents an o-, m- or p-xylylene group or a group of the formula:



in which D, G, v, z and u are defined as in claim 1.

3. A method according to claim 1 or 2, in which R is a methyl or hydroxyethyl radical, R' is an alkyl radical having 1 to 16 carbon atoms, a benzyl radical or a cyclohexyl radical, or R and R' together represent a polymethylene radical having 2 to 6 carbon atoms or the $\text{---}(\text{CH}_2)_2\text{---O---}(\text{CH}_2)_2\text{---}$ radical; A is a xylylene radical, a polymethylene radical having 2 to 12 carbon atoms which is optionally substituted by one or two alkyl radicals having 1 to 12 carbon atoms, or a radical of the formula:

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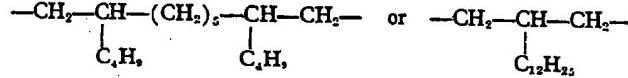
$\text{---}(\text{CH}_2)_n\text{---S---}(\text{CH}_2)_m\text{---}$, $\text{---}(\text{CH}_2)_n\text{---O---}(\text{CH}_2)_m\text{---}$, $\text{---}(\text{CH}_2)_n\text{---S---S---}(\text{CH}_2)_m\text{---}$, $\text{---}(\text{CH}_2)_n\text{---SO---}(\text{CH}_2)_m\text{---}$ or $\text{---}(\text{CH}_2)_n\text{---SO}_2---(\text{CH}_2)_m\text{---}$ radical; B is a polymethylene radical having 3 to 10 carbon atoms and is optionally substituted by one or two alkyl substituents having 1 to 12 carbon atoms, or is a xylylene radical, a $\text{---CH}_2\text{---CHOH---CH}_2\text{---}$ radical or a $\text{---}(\text{CH}_2)_n\text{---O---}(\text{CH}_2)_m\text{---}$ radical, n being 2 or 3, and X is a chlorine, iodine or bromine atom.

35

4. A method according to claim 1, in which R is a methyl radical, R' is an alkyl radical having 1 to 16 carbon atoms, a benzyl radical or a cyclohexyl radical, or R and R' together represent the $\text{---}(\text{CH}_2)_2\text{---O---}(\text{CH}_2)_2\text{---}$ radical, A is a xylylene radical or a polymethylene radical having 2 to 12 carbon atoms which is optionally substituted by one or two alkyl substituents having 1 to 12 carbon atoms; B is a polymethylene radical having 3 to 10 carbon atoms which is optionally substituted by one or two alkyl substituents having 1 to 12 carbon atoms, or a xylylene radical; and X is a chlorine, iodine or bromine atom.

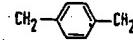
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5. A method according to claim 1, in which R=R'=CH₃, X=Br and A represents

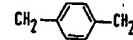


and B = $\text{---}(\text{CH}_2)_3\text{---}$; or

A = $-(CH_2)_2-$ and B represents $-(CH_2)_4-$, $-(CH_2)_6-$, $-(CH_2)_{10}-$ or



or A = $-(CH_2)_8-$ and B represents $-(CH_2)_4-$, $-(CH_2)_6-$, $-(CH_2)_{10}-$ or



5 or A = $-(CH_2)_6-$ and B represents $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_5-$,
 $-(CH_2)_6-$, $-(CH_2)_{10}-$, $-(CH_2)_2-\text{CH}-$, $-(CH_2)_3-\text{CH}-$ or



an o or p-xylylene radical; or

A = $-(CH_2)_8-$ and B = $-(CH_2)_4-$ or $-(CH_2)_6-$; or

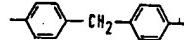
A = $-(CH_2)_{10}-$ and B = $-(CH_2)_4-$ or $-(CH_2)_{10}-$.

10 6. A method according to claim 1, in which R=R'=CH₃, X is an iodine atom,
A = $-(CH_2)_6-$ and B = $-(CH_2)_3-$.

7. A method according to claim 1, in which R and R' together represent the
 $-(CH_2)_2-\text{O}-(CH_2)_2-$ radical, X=Br, A represents $-(CH_2)_6-$ or $-(CH_2)_{10}-$
and B represents $-(CH_2)_3-$, or A = $-(CH_2)_8-$ and B = $-(CH_2)_6-$.

15 8. A method according to claim 1, in which R=R'=CH₃, X=Cl, and A =
 $-(CH_2)_6-$ and B = $-\text{CH}_2-\text{CHOH}-\text{CH}_2-$ or $-(CH_2)_2-\text{O}-(CH_2)_2-$, or
A = $-(CH_2)_8-$ and B = $-(CH_2)_2-\text{O}-(CH_2)_2-$.

9. A method according to claim 1, in which R=R'=CH₃, X=Br, and A =
 $-(CH_2)_2-\text{S}-\text{S}-(CH_2)_2-$ and B represents $-(CH_2)_6-$, $-(CH_2)_{10}-$,
 $-(CH_2)_8-$, $-(CH_2)_4-$, $-(CH_2)_3-$, $-(CH_2)_6-$, $-(CH_2)_{10}-$ or p-
xylylene; or A represents $-(CH_2)_3-\text{O}-(CH_2)_2-$ or p-xylylene; or A represents
 $-(CH_2)_3-\text{S}-\text{S}-(CH_2)_3-$, $-(CH_2)_2-\text{S}-(CH_2)_2-$, $-(CH_2)_2-\text{SO}-(CH_2)_2-$
or



25 25 and B represents $-(CH_2)_5-$; or

A represents $-(CH_2)_2-\text{O}-(CH_2)_2-$ and B represents a p-xylylene radical, a
 $-(CH_2)_2-\text{O}-(CH_2)_2-$ radical or a $-\text{CH}_2-\text{CHOH}-\text{CH}_2-$ radical; or

A = $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$, $-(CH_2)_{10}-$ or p-
xylylene and B = $-\text{CH}_2-\text{CHOH}-\text{CH}_2-$; or

30 30 A = $-(CH_2)_2-\text{SO}_2-(CH_2)_2-$, and B = $-(CH_2)_6-$.

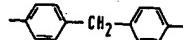
10. A method according to claim 1, in which R=CH₃, R'=C₄H₉ and A =
 $-(CH_2)_2-\text{S}-\text{S}-(CH_2)_2-$ and B = m-xylylene; or A = $-(CH_2)_{10}-$ and B =
 $-\text{CH}_2-\text{CHOH}-\text{CH}_2-$; or A=p-xylylene and B = $-(CH_2)_2-\text{O}-(CH_2)_2-$; or
R'=C₆H₁₃, and A = $-(CH_2)_2-\text{S}-\text{S}-(CH_2)_2-$ and B = $-(CH_2)_6-$; or
A = $-(CH_2)_6-$ and B = $-(CH_2)_2-\text{O}-(CH_2)_2-$; or R'=C₁₂H₂₅ and
A = $-(CH_2)_2-\text{S}-\text{S}-(CH_2)_2-$ and B = $-(CH_2)_6-$, or A = $-(CH_2)_8-$ and
B = $-(CH_2)_2-\text{O}-(CH_2)_2-$.

35 35 11. A method according to claim 1, in which R = $-\text{CH}_2-\text{CH}_2\text{OH}$, R' = CH₃
and A = $-(CH_2)_3-$ and B = $-(CH_2)_6-$, $-(CH_2)_{10}-$ or



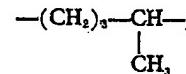
40 A=m-xylylene and B = $-(CH_2)_6-$; or R'=C₄H₉, A = $-(CH_2)_6-$ and B =
 $-(CH_2)_2-\text{O}-(CH_2)_2-$; or R'=C₆H₁₃, A = $-(CH_2)_6-$ and B = p-xylylene or
 $-\text{CH}_2-\text{CHOH}-\text{CH}_2-$; or R'=C₁₂H₂₅, A = $-(CH_2)_6-$ and B = $-(CH_2)_6-$; or
R and R' together represent the divalent radical $-(CH_2)_2-\text{O}-(CH_2)_2-$ or
 $-(CH_2)_6-$, A = $-(CH_2)_6-$ and B = $-\text{CH}_2-\text{CHOH}-\text{CH}_2-$.

45 45 12. A method according to claim 1, in which either R=R'=CH₃, X=Br and
A = $-(CH_2)_4-$ and B = $-(CH_2)_2-$, $-(CH_2)_4-$ or o-xylylenyl, or A = $-(CH_2)_5-$
and B = $-(CH_2)_2-\text{CH}-$, or A = $-(CH_2)_2-\text{O}-(CH_2)_2-$ and B = $-(CH_2)_3-$,
or CH₃ A =



50 50 and B = $-(CH_2)_2-\text{O}-(CH_2)_2-$ or $-\text{CH}_2-\text{CHOH}-\text{CH}_2-$, or A = p-xylylidetyl
and B = $-\text{CH}_2-\text{CHOH}-\text{CH}_2-$.

13. A method according to claim 1, in which R=CH₃, R'=n-propyl, X=Br and A=—(CH₂)₃— and B=—(CH₂)₄—, or A=—(CH₂)₅— and B=



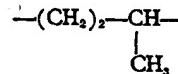
5 o-xylylenyl or —(CH₂)₄—, or A=m-xylylenyl and B=—(CH₂)₁₀—.

14. A method according to claim 1, in which R=CH₃, R'=isopropyl, X=Br, A=—(CH₂)₃— and B=—(CH₂)₅— or —(CH₂)₆—.

15. A method according to claim 1, in which R=CH₃, R'=benzyl, B=—CH₂—CHOH—CH₂—, and A=—(CH₂)₃— if X=Br and A=—(CH₂)₆— if X=Cl.

10 16. A method according to claim 1, in which R=CH₃, R'=C₄H₉, X=Br, A=m-xylylenyl and B=—CH₂—CHOH—CH₂—.

17. A method according to claim 1, in which R and R' together represent a —(OH₂)₃— group, X=Br, B represents —CH₂—CHOH—CH₂— and A represents



15 or m-xylylenyl.

18. A method according to claim 2 in which R is a C₁ to C₅ alkyl group.

19. A method according to any one of the preceding claims in which the polymer is applied in the form of an aqueous, alcoholic or aqueous-alcoholic solution, cream, gel or emulsion, or an aerosol containing a propellant.

20 20. A method according to any one of the preceding claims, in which the polymer is applied in the form of a composition containing from 0.5 to 10% by weight of polymer.

21. A method according to claim 19 or 20 in which the polymer is as defined in claim 4 or 18.

22. A method according to any one of the preceding claims in which the polymer is applied to the hair before an anionic and/or non-ionic shampoo or before an oxidation dyeing process followed by an anionic and/or non-ionic shampoo.

23. A composition suitable for application to the hair and/or skin which comprises at least one quaternised polymer as defined in any one of claims 1 to 18 and at least one cosmetic adjuvant which is:

(i) a cosmetic resin such that the composition is in the form of a hair lacquer or wave-setting lotion;

(ii) a hair dye;

(iii) a hair restructuring agent;

(iv) a surface-active agent such that the composition is in the form of a shampoo; or

(v) an oil such that the composition is in the form of an emulsion for application to the skin.

24. A composition according to claim 23 which is in the form of an aqueous or alcoholic solution containing a cosmetic resin.

25. A composition according to claim 23 which contains a cosmetic resin and an aerosol propellant.

26. A composition according to claim 23 which is in the form of a cream and contains a hair dye.

27. A composition according to claim 23 which contains an oil and is a cream, a sun-cream, a tinting cream or a cleansing milk.

28. A composition according to any one of claims 23 to 27 in which the polymer is present in an amount from 0.5 to 10% by weight.

29. A composition according to any one of claims 23 to 28 which contains at least one perfume, preservative, sequestering agent or thickener.

30. A composition according to any one of claims 23 to 29 in which the polymer is one specifically identified herein.

31. A composition according to claim 30 in which the polymer is one defined in claim 4 or 18.

32. A composition according to claim 23 substantially as hereinbefore described.

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33. A method according to any one of claims 1 to 22 which comprises applying a composition as claimed in any one of claims 23 to 32.
34. A method according to claim 1 substantially as hereinbefore described.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
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